GRAFT COPOLYMERIZATION OF VINYL MONOMERS ON NATURAL POLYMERS

THESIS

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To My Parents

Sh. Keshaw Prasad Pandey

&

Smt. Kamala Pandey

And

To The Memory of My Grandfather

Sh. Chandradhar Pandey

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Peeyoosh Kant Pandey

(PEEYOOSH KANT PANDEY)

CONTENTS

ABBREVIATION

PMS	→	Potassium Monopersulphate
PDP	→	Potassium Peroxydiphosphate
AA	→	Acrylic acid
ACM	→	Acrylamide
DOH	→	Dextran
AMPS	→	2-Acrylamido-2-methyl-1-propanesulphonic acid
NaCMC	→	Carboxy methylcellulose (sodium salt).
GOH	→	Guar Gum
TGA	→	Thermogravimatric analysis
PDT	→	Polymer Decomposition Temperature
FDT	→	Final Decomposition Temperature
IPDT	→	Integral Procedural Decomposition Temperature
TMEDA	→	N,N,N',N' - Tetramethylene Diamine
DSC	→	Differential Scanning Calorimetry
DTA	→	Differential Thermal Analysis
NMR	→	Nuclear Magnetic Resonance
MA	→	Mandelic Acid
XOH	→	Xanthan Gum

CHAPTER-I

Introduction

Macromolecular science has achieved a new dimension both in fundamental aspects as well as technological development since the inception of macromolecular concept about eighty years ago, due to the importance of macromolecules for meeting demands in specialized fields. In the present time in almost every field of human life polymers are being used. During the last three decades the study and application of biological activity of polymers have been developed. This development is a part of the growing need to design 'intelligent polymers', which extend the scope of polymeric materials. Synthetic macromolecules, however make up by for the largest and most diverse class of biomaterials[1,2]. The range of these polymeric materials is so wide that they have found application in practically every branch of industry and this makes them indispensable in modern world.

The first synthetic polymer utilized on a large scale was Bakelite produced by Bakeland in 1909. Since then, natural and modified polymers are being used extensively in the fields of pharmacology[3], diagnosis, dentistry, artificial respiration and in making articles of patient care. Commonly available material and synthetic polymers suffer from many disadvantages and therefore can not be used for special purposes. However, it is possible to modify a number of natural and commercially available synthetic polymers to give products, which can be utilized for performing desired functions.

The properties such as thermal stability and improvement in film strength, hygroscopicity, metal ion uptake, viscosity, ion exchange capacity, resistance to biodegradation, wettability, flocculation etc have been achieved by natural and synthetic polymers through graft co-polymerization[4-16]. These modified polymers called as graft copolymers have been found to be useful in oil recovery[17-19]. Graft copolymer of vinyl monomers bearing positive charge or episulfide groups onto certain fibres has recently been reported to possess antibacterial activity[20] Synthetic PMMA-grafted polysaccharides have been

used as hydrophilic matrix for controlled-release forms[21]. Solid phase grafting of 4-vinyl pyridine onto isotactic polypropylene has been successfully tried to impart latter special property[22]

Co-polymerization is the most general and powerful method of modification of polymers Co-polymerization modifies the polymer chain and modulates both the intermolecular and intermolecular forces and thereby the physical and chemical proportion.

In co-polymerization process two or more structurally different monomers are incorporated into the same polymer chain The properties of polymer synthesized by co-polymerization can be varied over a wide range by adjusting the monomer ratio Copolymers have linear, branched or cross-linked structures. Co-polymerization involves a definite chemical reaction between two monomers. Co-polymerization generally carried out by free radical method results in the formation of following different types of copolymers.

1. RANDOM COPOLYMERS:

The polymer composed of monomeric units M_1 and M_2 are arranged randomly

$$- M_1 - M_1 - M_2 - M_1 - M_2 - M_2 -$$

These copolymers are produced in bulk, solution, aqueous, suspension or emulsion using free radical initiators of the peroxide type or redox systems. Initiation through irradiation is also possible.

2. ALTERNATING COPOLYMRS:

The monomer units react with a high degree of order forming a polymer chain having a degree of alternation as in:

$$- M_1 - M_2 - M_1 - M_2 -$$

Special copolymerization techniques are used for synthesizing alternating copoymers. The reactivity of polar monomers can be enhanced by complexing them with metal halide or organo-aluminuim halide. These complexed monomers participate in one electron transfer reaction with either an uncomplexed monomer or another electron donar monomer.

3. BLOCK COPOLYMR:

Block copolymers are synthesized from two or more monomers in such a way that monomers of the same kind are arranged in groups or 'block', as in

$$- M_2 - M_2 - M_2 - M_1 - M_1 - M_1 -$$

Sequential anionic addition method, ring opening polymerization or step growth polymerization are the techniques by which block copolymers are synthesized.

4. GRAFT COPOLYMER:

There are macromolecules in which two or more macromolecular parts of different composition are joined chemically in such a way that one part forms the main chain and the other part, the side chain. The parts themselves are uniform polymerizates or polycondensates The structure of such copolymer may be represented as

$$\begin{array}{llllllll}
- M_1 & - M_1 - M_1 - M_1 & - M_1 & - M_1 - - & \text{polymeric back bone} \\
\ \ | & & \ \ | & & \\
M_2 & & M_2 & & \\
\ \ | & & \ \ | & & \\
M_2 & & M_2 - \text{Graft} & & \\
\ \ | & & \ \ | & & \\
M_2 & & & &
\end{array}$$

Schematic representation of graft copolymer

Random and alternating copolymers, prepared by polymerizing two kinds of monomers possess better properties than constituent homopolymer. On the other hand, graft and block copolymers exhibit many properties that are characteristics of each constituent homopolymer. The graft and block copolymer exhibit properties different either from random copolymer or a physical mixture of the constituent homopolymers Conditions are usually so chosen as to retain the desirable properties and to eliminate the less desirable properties of the individual block or graft components. By grafting, some new properties associated with the side chains are added without drastically changing the basic properties of the substrate polymer.

Graft co-polymerization induces the attachment of polymer chains formed by polymerization of one or several monomers onto a preformed backbone polymer. Polymerization of monomer onto backbone polymer takes place at active centers, which are generated by the chain transfer of growing chains of monomer. This mode of synthesis was first suggested by Flory[23] in 1937. The concept of graft co-polymerization was first introduced by Bandel and Alfrey[24], the term 'Graft' was adopted by other workers later on. The simplest case of raft copolymer can be represented by the structure-

$$\begin{array}{c} -M-M-M-\overset{}{X}-M-M- \\ \end{array}$$
$$\begin{array}{c} | \\ M_1 \\ | \\ M_1 \\ | \\ M_1 \end{array}$$

where sequence of monomer M is referred to as the main chain or backbone, the sequence of monomer M_1 is the side chain or graft and X is the active site in the backbone to which the graft is attached Thus the synthesis of graft co-polymerization involves the generation of ative sites on the polymeric backbone where grafting of different vinyl monomers can take place. The method, producing minimum amount of homopolymer and maximum amount of graft copolymer, is employed for generating active sites.

SYNTHESIS OF GRAFT COPOLYMERS

Synthesis and characterization of graft copolymers have received considerable interest in recent years due to its industrial importance. The chemistry of graft co-polymerization essentially involves the generation of active sites on the backbone polymer where appropriate monomer can be grafted. Different methods of activation include

1 Physical Activation

2. Chemical Activation

3 Radiation Activation

1. PHYSICAL ACTIVATION

Physical activation include application of stress to polymeric backbone swelling it with suitable solvents[25,26] etc Application of stress to polymeric backbone causes segmental motions and molecular flow, which may lead to bond scission and consequent formation of free radicals. Freezing and thawing of polymer monomer mixture also generates active sites[27]. Free radicals may also be generated by mastication and milling of the backbone polymer[28]. Production of a polymer with pendant basic moities was performed by grafting dimethylaminoethy-methacrylate to linear low-density polyethylene (LDPE) in the melt in a batch type internal mixer[29]

2. CHEMICAL ACTIVATION

This method of activation includes two different mechanism: -

(i) Free radical mechanism

(ii) Ionic mechanism

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(i) **Free Radical Mechanism:**

(a) ***Radical Initiator:***

In the presence of radical initiators such as Benzoyl Peroxide (BPO), azobisisobutyronitrile (AIBN), persulfates ($S_2O_8^{2-}$) cyanoxyl[30] etc. grafting of vinyl monomers onto polymeric backbones involves generation of free radicals by hydrogen abstraction and chain transfer processor as described below : -

$$I_2 \rightarrow 2\,I^{\bullet}$$

$$I^{\bullet} + PH \rightarrow P^{\bullet} + IH$$

$$I^{\bullet} + M \rightarrow IM^{\bullet} \xrightarrow{nM} I - Mn - M^{\bullet}$$

$$PH + I - Mn - M^{\bullet} \rightarrow P^{\bullet} + I - (M)_{n+1} - H$$

$$P^{\bullet} + M \rightarrow PM^{\bullet} \xrightarrow{nM} P - Mn - M^{\bullet}$$

$$P^{\bullet} + I - Mn - M^{\bullet} \rightarrow P - (M)_{n+1} - I$$

Where I_2 represents initiator molecule, PH is the polymer backbone and M is the vinyl monomer.

The extent of grafting is dependent on various reaction parameters, such as concentrations of initiator and monomer, reaction time, temperature etc. The nature of initiator and the monomer influences the reactivity of initiator and monomer towards grafting It has been observed by Mirre et al. that during grafting of vinyl monomers onto starch, wool or rubber, conventional free radical initators exhibit different reactivity toward grafting[31].

Although this process is not very efficient but it has received considerable importance because it is industrially important. The major drawback of this process is that it produces considerable amount of homopolymer. Therefore various radical initiators are employed to graft different vinyl monomers on natural and synthetic polymeric backbones so as to minimize the production of homopolymer.

(b) *Redox Mechanism:*

In redox initiation the free radical that initiate the polymerization are generated, as transient intermediates in the course of redox reaction. Essentially this involves an electron transfer process followed by scission to give free radicals A wide variety of redox reactions, involving both organic and inorganic components either wholly or in part, may be used for this purpose. These reactions take place in aqueous medium and occur rather rapidly, even at relatively low temperatures

The general mechanism of grafting involves an abstraction of the hydrogen atom from the backbone of the polymeric material by the transient radical formed during the redox reaction, thus generating macro radicals onto which the monomer molecules add to produce graft copolymer. There exists a number of redox systems that can initiate polymerization of vinyl monomers.

Peroxydisulfate System:

The activation of persulfates by various reductant viz. metals, oxidizable metals, metal complexes, salts of various oxyacid of sulfur, hydroxylamine, hydrazine etc has been reported[32-34)

The Ag^+ - $K_2S_2O_8$ is also very useful redox agent and the following mechanism for its decomposition was proposed by Bawn and Margarison[(35)]:

$$Ag^{+} + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^{2-} + SO_4^{-\bullet}$$

$$Ag^{2+} + S_2O_8^{2-} \rightarrow Ag^{3+} + SO_4^{2-} + SO_4^{-\bullet}$$

$$Ag^{3+} + 2OH^{-} \rightarrow Ag^{+} + 2OH^{\bullet}$$

Polyamide fibre was grafted with MMA using the peroxydisulfate Ag^+ redox system[(36)]. Other metals such as Cu^{2+}, T_i^{3+} and Co^{2+} have also been coupled with persulfate to form an effective redox system Potassium persulfate

with ferrous sulfate was successfully used as the initiator for grafting vinyl monomers onto wool[37] and Cellulose[38] by Misra et al.

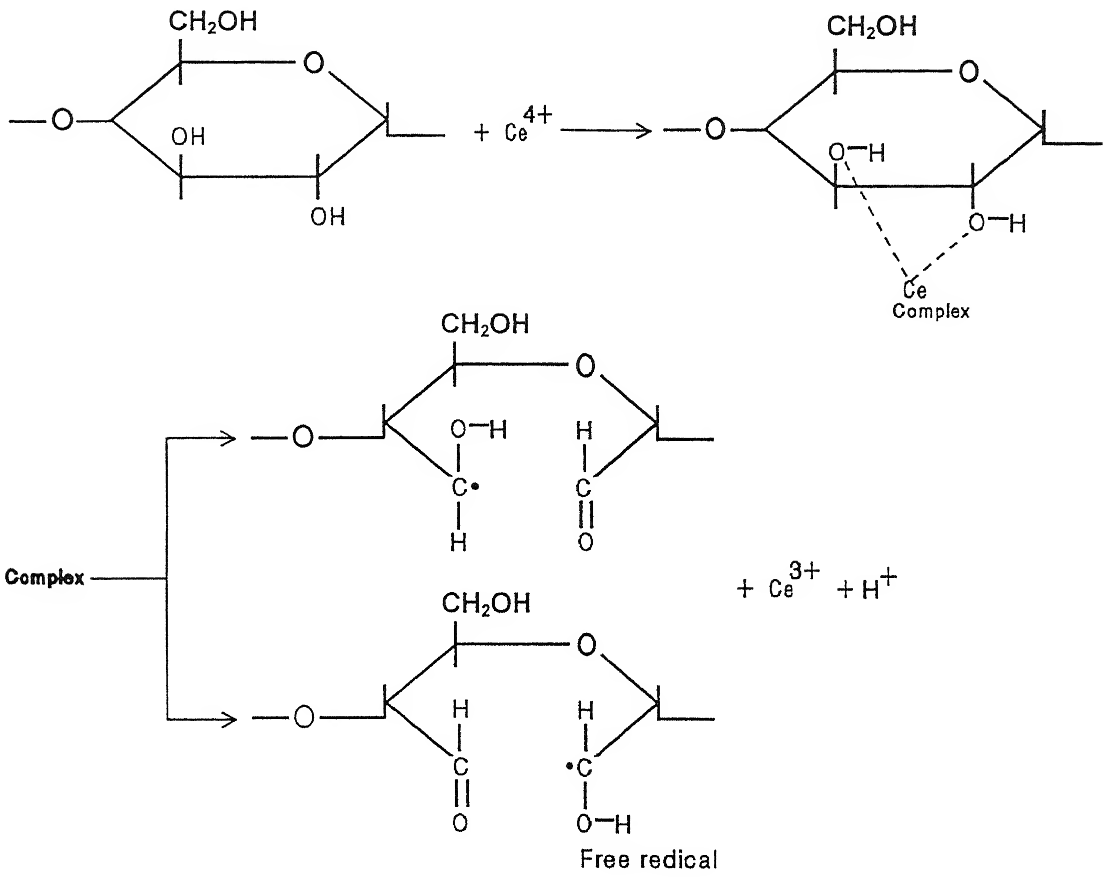
Peroxydiphosphate System:

In conjugation with Ag^+, V^{+5}, Co^{2+} and acid, peroxydiphosphate forms an efficient redox system for polymerization of vinyl monomers [39-45]. $H_2P_2O_8^{2-}$ is assumed to be an active species of peroxydiphosphate. The initiating species are OH° and $HPO^{-\circ}_4$ and the termination is considered to be exclusively by mutual method Nayak and Coworkers investigated the graft co-polymerization of methyl methacrylate onto silk[46] wool[47], Cellulose [48], Nylon[49] initiated by PDP coupled with various activators. The rate of grafting was determined by changing the concentration of monomer, activator, initiator, acidity of reaction medium and temperature. Behari, K and Coworkers have successfully carried graft copolymerization of vinyl monomers onto guar gum initiated by peroxydiphosphate coupled with various activators [50].

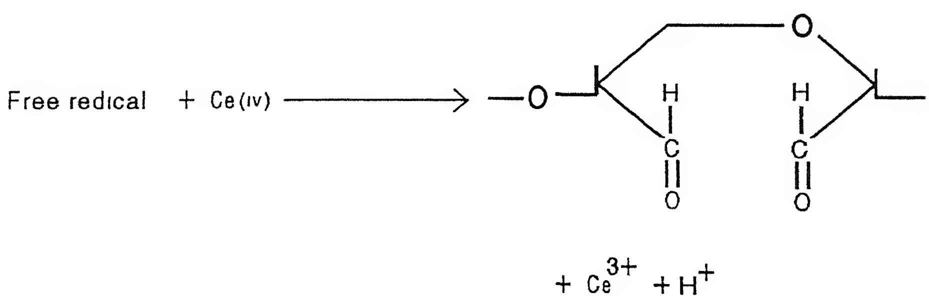
Ce^{4+} Redox System:

Following the findings of Mino and Kaizerman [51] that ceric ion can form a redox system with cellulose, grafting onto various natural polymers has been carried out by the ceric ion method With organic reducing agents such as alcohols certain ceric salts such as nitrate and sulfate form very efficient redox system. If a polymeric reducing agent, such as cellulose, is employed and the oxidation is conducted in the presence of vinyl monomers, graft copolymer formation will occur. This method of grafting of vinyl monomers onto cellulosic substrates. were extended by Mino et al. [52] and Stanett et al. [53]. Chowdhary et al. has successfully grafted methyl methacrylate onto polyvinyl alcohol using Ce^{4+} as initiator[54]

In the case of cellulose the reaction between ceric ion and cellulose occurs to produce active sites on cellulose in the following manner[55]:



Free radical + monomer → Graft copolymer



Ceric ion is capable of initiating polymerization of vinyl monomers[56] which can be written as

$$M + Ce^{4+} \rightarrow M^{\bullet} + Ce^{3+} + H^{+}$$

Where M = Vinyl Monomer

$$M^{\bullet} + M \rightarrow M_2^{\bullet}$$

$$M_{n-1}^{\bullet} + M \rightarrow M_n^{\bullet}$$

$$M_{n-1}^{\bullet} + Ce(IV) \rightarrow \text{Homopolymer} + Ce^{3+} + H^{+} \text{ (Termination)}$$

Therefore ceric ion initiated grafting may contain considerable amount of homopolymer along with grafted product

Metal Chelate Initiated Grafting:

A number of metal chalets containing transition metals in their higher oxidation states are known to decompose by one electron transfer process to generate free radical species, which may initiate graft co-polymerization reactions. Different transaction metals such as Zn, Fe, V, Co, Cr, Al etc. have been used in the preparation of metal acetyl acetonates and other diketonates. Several studies demonstrated earlier that metal acetyl acetonates can be used as initiators for vinyl polymerization Few studies have been reported on the use of metal chelates as initiators for grafting. However, in recent years grafting of wide variety of vinyl monomers onto wool and cellulose by the use of metal chelates has been reported [57-58]

Hydrogen Peroxide Reductant System:

Combination of H_2O_2 and Fe(II) salts, generally known as 'Fenton Reagent' have for many years been used in organic and polymer chemistry. The use of Fe^{2+}/H_2O_2 as an effective redox pair for grafting vinyl monomers onto preformed macromolecules was reported by Rogivin and Co-workers [58-63]. These authors [64] and Ogiwara et al. [65] suggested that the decomposition of

hydrogen peroxide by ferrous ion (Fe^{2+}) is a typical redox reaction for producing OH° radical that initiate grafting-

$$HO\text{-}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet}$$

Hydroxyle radical can abstract hydrogen from polymeric substance molecule containing -OH, -COOH etc as pendant group to produce active sites where vinyl monomers can be grafted

$$S + OH^{\bullet} \rightarrow S^{\bullet}$$

$$S^{\bullet} + M \rightarrow \text{graft copolymer}$$

Where S stands for substrate.

Fenton reagents have been used in numerous graft co-polymerization reactions Mishra et al. have utilized Fenton reagent as initiator for grafting vinyl monomer onto Wool [(65)] and Cellulose [(67-68)] and observed that the molar ratio of $[Fe^{2+}]/[H_2O_2]$ influences percentage of grafting.

Quinquevalent Vanadium (V^{+5}) System:

In a quantitative survey Waters and Littler [(69)] reported the oxidation of a multitude of organic substances (alcohols, acids, amines etc.) by quinquevalent vanadium (V^{+5}) in aqueous sulfuric acid. These oxidations were found to proceed through free radical path that effectively initiates vinyl polymerization [(70-74)]. Quinquevalent vanadium has a similar affinity towards polymeric substrates containing pendant groups (-OH, -CHO, -$CONH_2$, -COOH etc.) on their back bone. Interaction of V(V) with these pendant groups results in the formation of free radical sites on the polymer backbones. These macro radical attack vinyl monomers at immediate vicinity, resulting in the formation of graft copolymers without simultaneous formation of homopolymer as has been reported by Rogovin et al [(74)] in the synthesis of dialdehyde cellulose-g-polyacrylonitrile, polyacrylamide-g-poly (2-methl-5-vinyl pyridine) etc

In a system containing V^{+5}, monomer activator and polymer substrate where grafting has to take place, V^{+5} may interact with the activator (R) to form complex that dissociates in a unimolecular fashion giving rise to primary free radicals These radicals along with V^{+5} abstracts hydrogen from the polymeric substrate to yield free radical sites to which monomer addition takes place resulting in graft copolymer. The mechanism can be represented as.

$$V^{-5} + \underset{\text{activator}}{R} \rightleftharpoons \text{Complex} \rightarrow R^{\bullet} + V^{+4} + H^{+}$$

$$SH + R^{\bullet} \rightarrow S^{\bullet} + RH$$

Where SH is polymeric backbone.

$$SH + V^{+5} \rightarrow \text{Complex} \rightarrow S^{\bullet} + V^{+4} + H^{+}$$

$$S^{\bullet} + M \rightarrow SM^{\bullet}$$

$$SM^{\bullet}_{n-1} + M \rightarrow SM^{\bullet}_{n}$$

$$SM^{\bullet}_{n} + SM^{\bullet}_{m} \rightarrow \text{graft copolymer}$$

Potassium Monopersulfate ($KHSO_5$) Initiation:

Kennedy et al [75] for the first time reported the versatile oxidising action of $KHSO_5$ in the oxidation of organic substrates for preparative purpose. It is found to be effective in causing high rate of initiation in vinyl polymerization[76-80] and graft co-polymerization of vinyl monomers onto cotton, cellulose[81-82], Jute[83-84] dextran[85] and wool fibres[86-88]. The effect of various reaction components such as concentration of salts, complexing agents, $KHSO_5$, mineral acids, monomers, reaction time, temperature and organic solvents on the rate of vinyl polymerization has been studied. $KHSO_5$ coupled with salts of Fe^{2+} is also an effective redox pair for effective graft co-polymerization.

Ionic Mechanism

Ionic grafting methods are used for selective generation of active sites on backbone. Ionic grafting may be -

(a) Cationic Grafting (b) Anionic Graftng

(a) ***Cationic Grafting:***

The initiation reactions between labile alkyl halide and various Lewis acids[89,90] have been utilized for cationic grafting of halogenated backbone polymer[91,93]. The grafted monomers include styrene, alkyl vinyl ethers, tetrahydrofuran and isobutylene.

(b) ***Anionic Grafting:***

Considerable work on grafting by anionic polymerization has been reported in literature. Halogenated polymeric backbone can react with metals and organo-metallic compounds to generate carbanionic sites for grafting[94]. A very efficient method for generating carbnionic grafting sites on polymeric backbones utilizes an alkyl lithium compound complexed with N, N, N', N' - tetramethylene diamine (TMEDA) to metalate allylic, benzylic and aromatic C-H bonds[95]. Polybutadiene and polyisoprine have been grafted with styrene [96,97]. Menashe et al [98,99] carried out anionic graft co-polymerization of acrylonitrile and methacrylonitrile onto potassium alkoxide derivative of starch.

Radiation-Induced Graft Co-polymerization

Grafting by means of radiation is by far the most popular synthetic technique for modification of polymers and the majority of the literature on graft co-polymerization describe the use of a radiation method in some form or another This method is based on the principle that when electromagnetic radiations are passed through the matter, the intensity of radiations decrease and

the absorbed radiations activate the polymeric backbone. Various methods have been used for effecting grafting by using high-enough radiations[100,101].

CHARACTERIZATION OF GRAFT COPOLYMER

Different parameters such as percentage of grafting or grafting ratio (%G), percentage efficiency(%E), percentage add on(%A), percentage conversion(%C) and percentage homopolymer(%H) are usually determined as functions of different variables that influence graft co-polymerization, according to Fanta's definition[102].

$$\text{Grafting Ratio (\% G)} = \frac{\text{Grafted Polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Grafting Efficiency (\% E)} = \frac{\text{Grafted Polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Add on (\% A)} = \frac{\text{Synthetic Polymer}}{\text{Graft Copolymer}} \times 100$$

$$\text{Conversion (\% C)} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Homopolymer (\% H)} = 100 - \text{\% E.}$$

These parameters give the quantitative measurement of the grafting reaction The general characterization of the graft copolymer is based on the following

1) Spectroscopic Measurements:

The formation of graft copolymer can be established by taking IR spectra of the original backbone polymer and the grafted polymer. The grafted polymer would show the additional peaks due to the pendant groups present in the grafted polymer. Techniques like NMR, ESCA and X-ray diffraction too have been used to characterize the graft copolymers.

2) Thermal Analysis:

Thermal studies of the graft copolymers and the backbone polymer show a marked difference in their thermal behaviour, which suggests that upon grafting the properties of the grafted polymer are changed. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), differential thermogrvimetric analysis (DTG), are different methods of characterizing the graft copolymers.

Thermogravimetric analysis (TGA) is defined as a continuous process that involves the measurement of sample weight as the reaction temperature is changed by means of a programmed rate of heating. Graft copolymers are subjected to thermal studies in order to characterize and to know their usefulness towards particular objective[103,104]. Thermogravimetric analysis in inert atomosphere is also used as a method for emperically asserting the thermal stabilities of experimental polymer Many factors can affect the thermal stability of polymers. There are melting or softening points, bond strengths, activation energies, crosslinking and the presence of low molecular weight, volatile materials, weak links and groups which are readily affected by heat etc. in order to properly assess the thermal stability of polymers. These factors must be simultaneously considered. Since this is virtually impossible, various investigators have devised arbitrary qualitative and quantitative methods such as:-

(a) Qualitative Methods.

(b) Semiquantitative Methods.

(c) Quantitative Methods.

Qualitative Methods:

It is often possible, merely by visual observation, to ascertain the relative thermal stabilities of various polymers. Jeffreys[105], in order to

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establish a criterion for evaluating the resin (phenolic) decomposition, suggested for recording the temperatures at which 10% decomposition and 50% decomposition occured. Temperature at which rate of decomposition is maximum (T_{max}) is also recorded and is helpful in predicting the thermal stability of polymer.

Recently Horowitz and Perros[106,107] discussed the thermal stability of certain polymers. In a plot of weight loss vs. temperature, after an initial weight loss, a sharp break occured indicating, the onset of decomposition process involving a rapid loss of volatile fragments. As a measure of stability, decomposition temperatures of a polymer are determined. This involves drawing straight lines through the experimental points on the expanded thermogram before and after the initial sharp break in the curves that occur at moderately low weight losses. The intersection of these two lines is then projected on the temperature axis and this temperature is defined as the polymer decomposition temperature (PDT).

Semiquantitative Methods:

Doyle[108,109] has proposed indexes of thermal stability in terms of decomposition temperatures. Since the values of these indexes depend upon many 'procedural' decomposition temperature'. Two types of such temperatures have been defined for TGA traces in inert atmosphere. One of these is called 'differential procedural decomposition temperature (DPDT) and the other the integral procedural decomposition temperature (IPDT). However, since many materials decompose in steps, the DPDT is neither a unique emperical end point nor a consistently unambiguous index of incipeint degradation, therefore, it is not in much use.

The second type of index, IPDT, is used as a way of summing up the whole shape of the normalized data curve. As such, it is readily available and

is highly reproducible. In order to place materials on an equal procedural basis, the total experimentally accessible temperature range from 25 to 900°C has been employed. IPDT is calculated[109] by the following equation:

$$IPDT = 875A^*K^* + 25$$

A^* and K^* are calculated with the help of the following equation.

$$T^* = 875A^* + 25$$

In this expression it was assumed that all materials volatilize completely below 900°C and so at a single temperature. The value of T^* serves as a crude measure of refractoriness; however many materials which possess high refractory weight fractions up to 900°C begin to decompose at much lower temperture.

Quantitative Methods:

The isothermal 'life' of a polymer may be quantitatively correlated with TGA curves. Thus Doyl[110] has obtianed an equation.

$$\log t_i \approx -\frac{E}{2.3\,RT} + \text{Constant}$$

based upon various simplifying assumption. In this equation t_i is isothermal aging time and T is absolute thermogravimetric analysis temperature corresponding to equivalent aging time t_i.

3) Scanning Electron Microscopy:

Deposition of the polymer grafted into the preformed polymer backbone can be characterized by scanning electron microscopy (SEM). Misra et al. have studied the scanning electron micrographs of wool, grafted wool[111,112]

cellulose, grafted cellulose, starch [113] and grafted starch [114] and found that a considerable amount of the grafted polymer is deposited on the respective polymer backbones.

REFERENCES

1. Hode, C.W.; *J Polym Sci.,* **B-3**, 573 (1965).

2. Hode, C.W., *J Polym Sci.*, **A-24**, 227 (1966).

3 Quchi, T., Hirano, T., Maruhashi, S.; Nishizawa, H.; Shizuno, K.; Ohya, Y.; *Polymer Preprint* **41(2)**, 1548-1549 (2000).

4. Hummel, D.O.; *J Polym Sci., Polymer Symp;* **67**, 169 (1980).

5. Sperling, L.H , (ed) *'Recent Advances in Polymer Blends, Graft and Blocks'.* Plenum Press, New York, **1974.**

6. *'Graft co-polymerization of Lignocellulosic fibres'* Edited by David N.S. Hon., *ACS Symp Series*, **187** (1982).

7. Ranby, B. and Zuchowska, D.; *Polym J.* **19**(5), 623 (1987).

8 Medicals Polymers, Chemical Problems, 'Proceedings of the 17th Prague IUPAC Microsymposium on Macromolecules' Prague Czechoslovakia (1977) Ed. by Sedlaceak, B.; Overberger, C.G.; Mark, H.F.; *J. Polym. Sci , Polym Symposium,* **66** (1979).

9. Sakamoto, M.; Hasuike, H.; Itoh, M.; Ishizuka, Y.; Yoshida, K.; Watamoto, , H., Furuhata, K.; *Cellul Chem., Biochem Mater. Aspects,* 391-6 (1993).

10. Iyer, V.; Varadarajan, P.V.; Sawakhande, K.H.; Nachane, N.D.; *J. Appl. Polym. Sci.***39** (11-12), 2259 (1990).

11. Miyata. N ; Sakata, I.; *Jpn. Kokai Tokkyo Koho J.P.* **6397,** 612 (1988).

12 Takagi, T ; Nitta. A.; Ito. H.; Nagai, K.; *Jpn Kokai Tokkyo Koho J.P.* 01,252,610 [89, 252, 610] (1988).

13 Saito, T., Sesaki, M.; Majaude, Y.; *Jpn Kokai Tokkyo Koho J.P.* 61,101,506 [86, 101, 506] (1986).

14. Ghosh, P.; Biswas, S.; Datta, C.; *J Mater. Sci.* 24(1), 205 (1989).

15. Tripathi, T.; Karmakar., N.C.; Singh, R.P., *Int. J. Polym. Mater.* **46 (1-2),** 81-93 (2000).

16. Yazdani-Pedram, M ; Retwert, J.; *Mater Res Soc Symp Proc.* **550** (Biomedical Materials-Drug Delivery, Implants and Tissue Engineering), 29-34 (1999).

17. Leansheng, Z.; *Eur Pat Appl. E P.* **356**,241 (1990).

18. Meister John. J., *U S* **454**,889,902 (1989).

19. Zhang, Li-Ming; Tan, Ye-Bang; Li, Zhuo-Mei; *J. Appl. Polym Sci.*, 77**(1)**, 195-201 (2000).

20. Nonaka, Takamasa; Noda, Eishiroh; Kusihara, Seiji; *J Appl. Polym. Sci.*, 77**(5)**, 1077-1086 (2000).

21. Castellano, I.; Goni, I.; Ferrero, M.C.; Munoz, A.; Ji Menez-Castellanos, R.; Gurruchaga, M.; Drug Dev. *Ind. Pharm.*, **25 (12),** 1249-1257 (1999).

22 Brahmbhatt, Rajesh B.; Patel, Alpesh C.; Jain, R.C.; Devi, Surekha; Eur. *Polym. J* ; **35**(9), 1695-1701 (1999).

23. Flory, P.J.; *J Am Chem Soc.* **59**, 241 (1937).

24. Alfray and Bandel, D ; Paper presented at *118th Am. Chem. Soc. Meeting, Chicago. Sept . 4 (1950)* through H. Mark *Rec. Chem. Progr.* 12(3), 139, (1951).

25 Kenokh, M.A.: *Zhur observer Rhim* **11**, 776 (1941).

26. Sparrow, A.H. and Rosenfled, F.M.; *Science* **10**4, 243 (1946).

27. Williams, J.L. and Stanett, N.J.; *Polym. Sci.* **B-8**, 711 (1970).

28. Deters, W and Huang, D., F*aserforsch Textile Tech.* **14(5)**, 183 (1963).

29. Simmons, A. and Baker, W.E.; *Polym. Eng. Sci*. **29(16)**; 1117 (1989).

30. Ghanou, YVes; Grande, Daniel, Gurrero, Ramiro, *Pohym. Pro* **40(2)**, 99-100 (1999).

31. Mishra, B N.; Dogra. R ; Kaur, I.; Sood, D.; *J Polym. Sci Polym. Chem.* Ed., **18** : 341 (1980).

32. Palit, S.R ; and Guha, T.; *J. Polym Sci* , **A-1** 1877 (1963).

33. Okamura, S. and Motoyama, T.; **J. Polym. Sci.** *58*, 221 (1962).

34. Verma, D.S. and Sarkar, R.K.; *Angew Markomol Chem*. **37**, 167 (1974).

35. Bawn, C.E.H. and Margarison; *Trans Faraday. Soc*. **51**, 925 (1955).

36. Lenka, S., *J Appl Polym Sci.* **27(6)**, 2295 (1982).

37. Mirsa, B.N.; Dogra, R.; Mehta, I.K. and Singha, A.S.; *Die Ang. Makromol Chemie*, **90**, 83 (1980).

38. Misra, B.N.; Mehta, I.K.; Khetarpal, R.C.; *J. Polym. Sci. Polym. Chem. Ed* **22**, 2767 (1984).

39. Behari, K . Das, R.; Agrawal, U.; *J. Polymer Sci.* **31**, 1449 (1993).

40. Behari, K.; Das R.; *Polym J.* **25 (10)**, 1007 (1993).

41. Behari, K.; Agrawal, U.; Das, R.; Bahadur, L.; *J. Macromol. Sci., Chem.* **A31(3)**, 383 (1994).

42. Behari. K; Agrawal, U.; Das, R.; Bahadur, L.; *Polymer Preprint* **31(1)**, 117 (1994).

43. Behari. K.; Das. R ; Agrawal, U.; Bahdur, L.; *Polymer*. **37(6)**, 1023 (1996).

44. Hariharan, S.S. and Meenakshi, A ; *J. Polym Sci. Polym Lett. ed.* **15,** 1 (1977).

45. Nayak, P.L.; Lenka, S. and Dhal, A.K.; *J. Makromol. Chem. Rapid Commun* **1**, 313 (1980).

46. Nayak, P.L.; Lenka, S ; Mishra, M.K.; *J Polym. Sci. Polym Chem. Ed.* **18**, 2247 (1980).

47. Nayak, P.L.; Lenka, S. and Mishra, M.K.; *Angew. Makromol Chem.* **90,** 155 (1980)

48 Nayak, P L.; Lenka, S.; Mishra, M.K.; *J. Appl. Polym. Sci.* **26,** 3151 (1981).

49. Dash, S.B.; Pradhan, A.K.; Pati, N.C. and Nayak, P.L.; *J. Macromol. Sci. Chem.* **A19(2)**, 343 (1983).

50 (a) Behari, K.; Taunk, K.; *J. Appl Sci.* **77**, 39-44 (2000).
   (b) Behari, K., Taunk, K.; *Ind. J. Chem Tech.* **4(3)**, 141 (1997).
   (c) Behari, K.; Taunk, K.; Tripathi, M.; Kumar R.; *Polym. Int* 49 153-157 (2000).

51. Mino. G. and Kaizermann, S.; *J. Polym. Sci.*, **31** 242 (1958).

52. Mino. G.; Kaizermann, S. and Meinhold, F.; *Textile Res. J* **32,** 136 (1962).

53. Stanett, V.; Schwab, E, Rakowitz. D.H. and Magrane, J.K.; *Tappi* **45**, 390 (1962).

54. Chowdhury, P.; Banerjee, M.; *J Appl. Polym. Sci,* **70(3)**, 523-527 (1998).

55 Gugliemelli, L.A. and Russel, C.R.; *J Polym. Sci ; Polym. Letters,* **9,** 711 (1971).

56. Mino., G.; Kaizermann, S., *J Polym. Sci.* **3,** 242 (1958).

57. Mısra, B.N., Jassal, J.R. and Dogra, R.; *J Macromol. Sci. Chem* **A16(6),** 1093 (1983).

58. Lı , Pei; Lıu, Jiany Hong; Wang, Qun, Wn, Che, *Macromol Symp,* **151,** 605-610 (2000)

59 Gulına, A A , Livshits, R.M and Rogovin Z.A.; *Polym. Sci.; USSR* **7,** 1247 (1965)

60 Maltseva. T.A.; Snezhko, D.L.; Virık, A.D.; Rogovin, Z.A.; *Izv Vyssh Uchebn, Zaved Khim Khım Tekhmol.* **8(4),** 651 (1960).

61. Korotkova. A Ya and Rogovın, Z.A., *Vysokomol Soedin* **7,** 1571 (1965).

62. Morin. B.P.; Yu G. Krya Zhen and Rogovin Z.A.; *Vysokomol Soedin* **7(8),** 1463 (1965).

63. Gulina, A.A , Lıvshit, R.M. and Rogovin Z.A.; *Polym. Sci. USSR* **7(7),** 1247 (1965)

64. Kubota, H. and Ogiwara, Y.; *J. Appl Polym Sci. 13*, 1569 (1965).

65. Samal. R.K.; Sahoo., P.K. and Samantray, H.S.; *J. Macromol. Sci.. Macromol, Chem Phys* **C26(1),** 81 (1986).

66. Mısra. B.N.; Chandel, P.S. and Dogra, R.; *J Polym Sci Polym Chem. Ed* , **16**, 1801 (1978)

67. Misra. B N.; Dogra, R.; Kaur, I. and Jassal, J.K.; *J Polym Sci. Polym. Chem Ed* , **17**, 1861 (1979).

68. Misra. B.N.; Dogra, R ; Mehta, I.K.; *J Polym Sci. Polym. Chem. Ed.* **18,** 749 (1980).

69. Waters. W.A. and Littler. J.S ; *in Oxidation in 'Organic Chemistry' Part A Ed* by Wıberg. K.B. **186** (1965).

70 Saccubaı. S. and Santappa. M.; *Makromol. Chem.* **117**, 50 (1968).

71. Saccubai, S. and Santappa, M ; *J Polym Sci* **A-1,** 7, 643 (1969).

72. Saccubai, S. and Santappa, M.; *Proc Indian Acad Sci.* **71,** 111 (1970).

73. Samal, R.K., Nayak, M.C.; Das, D.P. and Suryanarayan, G.V.; *Eur, Polym J* **17(9),** 1005 (1981).

74 Samal, R K., Das, D.P., Nayak, M.C. and Suryanarayan, G.V.; *J Macromol Sci Chem* **A15(3),** 467 (1981).

75. Rogovin, Z.A. and Livshits, *Vysoko Molekul. Soedin* **4(5),** 784 (1962).

76. Kennedy, R.J. and Stock, A.M., *J Org. Chem* **25,** 1901 (1960).

77. Samal. R.K.; Sahoo, P.K. and Bhattacharyajee, S.P.; *J. Macromol. Sci. Chem* **A23,** 2, 203 (1986).

78. Samal. R.K.; Samantray, H.S. and Samal. R.N.; *J. Ind. Chem. Soc. LXIV*, **547,** (1987)

79. Samal. R K., Samal, R.N. and Send, S.; *J Polym Material,* **8,** 207 (1991).

80. Samal, R.K.; Samantray, H.S. and Sahoo, P.K.; J. *Appl Polym. Sci.* **32,** 5693 (1986).

81. Samal. R.K.; Samantray, H.S. and Sahoo, P.K.; Samal. R.N.; Bhattacharyajee. S.P.; *J Polym. Material* **4,** 3165 (1987).

82. Samal. R.K.; Samantray, H.S. and Samal, R.N.; *J Appl Polym.* **37,** 3085 (1989).

83. Samal. R.K.; Samantray, H.S.; Samal, R.N.; *J. Polym Material,* **6,** 223 (1989).

84. Samal. R.K.; Dash. S. and Samantray, H.S.; *Indian J. Text Res.* **14(4),** 187 (1989).

85. Samal. R.K ; Samal, R.N. and Send, S.; *J. Polym Material,* **7,** 175 (1990).

86. Samal, R.K.; Sahoo, P K ; Giri, G ; *J. Appl. Polym. Sci.*, **40**, 471 (1990).

87. Samal, R.K., Nanda, C N. and Giri, G.; *J Polym. Material,* **7**, 209 (1990).

88. Samal R.K.; Giri, G.; *J Appl Polym Sci.* **42**, 2371 (1991).

89. Kennedy, J.P.; *J Macromol Sci. Chem* **3**, 86 (1961).

90. Kennedy, J.P. and Rangachary, S.; *Adv Polym. Sci* , **14**, 1 (1974).

91. Kennedy, J.P.; Plamthrottam S.S. and Ivan, B. *J; Macromol Sci. Chem.* **17**, 637 (1982).

92. Lehmann, J. and Dreytuss, P.; *Adv. Chem Ser.* **176**, 587 (1979).

93. Kennedy, J.P and Matzlar, D.K.; *J. Appl Polym Sci. Polym. Symp.* **30**, 105 (1977).

94. Bywater, S.; *Prog Polym Sci.* **4**, 27 (1974).

95 Polyamine Chelated Alkali Metal Compounds *Adv Chem. Sci.* **140** (1974).

96 Halasa, A.F.; Mitchell, G.B.; Stayer, M.; Tale, D.D.; Oberstar, A.E. and Koch, R.W., *J Polym. Sci. Polym. Chem Ed.*, **14**, 497 (1976).

97. Falk, J.C.; Van Fleet, J.; Hoeg, D.F.; Pendleton, J.F.; Schlott, R.J.; *Macromol Synth* , **8**, 57 (1982).

98. Menashi, T.; and Albert, Z.; *Eur. Polym. J.* **5(4)**, 499 (1969).

99. Menashi, T. and Albert, Z.; *J. Polym. Sci* **A1, 7(7)**, 1839 (1969).

100 Zhang, Sheng, Wang, Jiang, Ding, Yanbing; Wu, Shaoli; Xie Liging, Wen, Chenlin; *Chem Sci. Bull.,* **45(4)**, 322-325 (2000).

101. El-Boony, H.A., *Al-Azhar Bull Sci.*, **9(2)**, 517-525 (1998).

102. Fanta, G.F., *'Block and Graft Co-polymerization'*, R.J. Ceresa Ed., Wiley Inter Science New York **(1973)**, p.1.

103. Athawale, Vilas D.; Lale, VidyaGuare; *Starch/Starke,* **52(6-7)**, 205-213(2000)

104. Wilkie, Charles A.; *Polym. Degrad. Stab.* **66(3),** 301-306 (1999).

105. Jeffreys, K.D.; *Brit Plastics* **36,** 188 (1963).

106. Horowitz, E. and Perros, T.P.; *J.Inorg. Nucl. Chem.* **26,** 139 (1964).

107. Harowitz, E. and Perros, T.P.; *J. Res. Nail. Bur. Std.* **69 A,** 53 (1965).

108. Doyle, C.D ; *WADD Tech. Rept.* **60-283,** June 1960.

109. Doyle, C.D.; *Anal. Chem.* **33,** 77 (1961).

110. Doyle, C.D.; *J Appl Polym Sci.* **6,** 639 (1962).

111. Sood, D.S. and Misra, B.N ; *J. Macromol Sci Chem.* **A21 (10),** 1267 (1984)

112. Sood, D.S.; Kishore, J. and Misra, B.N.; *J. Macromol. Sci. Chem* **A22(3),** 263 (1985).

113 Misra, B.N., Dogra, R., Mehta, I.K. and Kiran Dip Gill; *J. Appl. Polym. Sci* , **26,** 3789 (1981).

114. Misra, B.N. and Dogra, R.; *J Macromol Sci Chem.* **A14(5),** 763 (1980).

CHAPTER-II

Graft Co-polymerization of Acrylamide/Acrylic acid onto Xanthan Gum

1. Structure, Chemical Composition, Properties and Uses of Xanthan Gum.

2. Graft Co-polymerization of Acrylamide onto Xanthan Gum by Fe^{2+}/BrO_3^- Redox Pair.

3. Graft Co-polymerization of Acrylic acid onto Xanthan Gum by Potassium monopersulphate (PMS)/Fe^{2+} Redox Pair.

1. STRUCTURE, CHEMICAL COMPOSITION, PROPERTIES AND USES OF XANTHAN GUM

Structure:

The mol-wt. of xanthan gum is (2-15)x10^6 [1-2]. The structure of xanthan gum consists of a β-(1→4)-linked D-glucopyranoryl backbone chain, *eg.* in cellulose (fig.2 1). To the chain are appended trisaccharide side chains composed of D-mannopyranosyl (Man) and D-glucopyranosyluronic acid (GlcA) residues[3-4]. The β-(1→2)-linked mannosyl residues have 6-O-acetyl substituents. An average of about half of the β-D-mannosyl end groups bear 4,6-O-(1-carboxyethylidene) substituents; i.e. 4,6-acetal-linked pyruvic acid. Although the indicated distribution of side chains reflects average values, it is in accordance with evidence for repeat-unit structure in microbial hetero-polysaccharides[5] and with the sharp temperature transition in optical rotation displayed by depyruvylated xanthan gum as contrasted with the broad transition displayed by the native gum[6].

Many of the properties of Xanthan gum dispersions indicate that the molecule assumes a rodlike, ordered secondary structure. A sharp increase in the viscosity of 0.5-1% aqueous dispersions has been noted at 50-60°C[7] and has been confirmed by optical rotation[8], circular dichroism[9], and nmr measurements[9]. Increasing the ionic strength raises the temperature at which the transition occurs; such melting out or denaturation is a helix-to-coil conformational transition which is similar to that observed for double-stranded nucleic acids, triple-stranded collagen, and certain polysaccharides[10]. X-ray diffraction studies with xanthan gum fibres indicate a helix of five fold symmetry with side chains folded along the backbone in a hydrogen-bonded structure[11]. Weak, noncovalent associations between aligned molecules build up a tenuous gel-like network responsible for the observed yield stress of xanthan gum dispersions.

Properties:

Aqueous dispersions of Xanthan gum exhibit several novel and remarkable rheological properties[12-14]. Low concentrations of the gum have relatively high viscosities which permits its economical use in applications, eg. emulsions stabilization and mobility control of water-flooding fluids in petroleum reservoirs. Xanthan gum solutions are characterized by high pseudoplasticity.

The viscosity is independent of pH from pH 1.5 – 13.0[14], when measured in the presence of salt in the solution Viscosity also is stable to heat over a wide temperature range, and this stability is enhanced by salts of mono and divalent cations[15]. In addition to psuedoplatic behaviour, xanthan gum solutions of 0.75% concentration or greater, display rheological yields that are characteristic of plastic dispersions, i.e. a tendency not to flow at ultra-low shear stress[16]. The yield value for xanthan gum in aqueous dispersion is increased in the presence of a salt[17].

Although xanthan gum is a polyelectrolyte by virtue of ionizable carboxyl groups belonging to D-glucuronic acid residues and pyruvate acetal, the viscosity of ca 0.35% solutions is virtually unaffected by the presence of 0.01-1% salt (KCl) concentrations. The presence of salt slightly increases viscosity for gum concentration higher than 0.35% and slightly lowers it for concentrations below this amount. Xanthan gum retains its water-binding and rheological properties in dense or saturated salt solutions [18].

Xanthan gum is produced industrially as well as with the help of certain bacterium. Both the processes involve fermentation of carbohydrate. The wide variety of nitrogen and carbohydrate sources can be employed for this purpose[19-21]. The first nitrogen source used in the process was dried distillers' solubles. Polysaccharide production by xanthomonas compestris growing in a chemostat culture on various limiting nutrients has been studied[22].

Uses:

It has been estimated that over half of microbial polysaccharide sales are in to the food industry(23). Food and pharmaceutical applications take advantage of properties e.g. thickening, emulsion stabilization, water-binding, suspending, salt and acid compabilities(24). The reversible, shear-thinning property imparts good mouth feel i.e. addition of gum does not alter the characteristic texture of the food in the mouth(25). Xanthan gum also interacts synergistically with galactomannans, e.g. locust bean and guar gums, to produce combined viscosities greater than would be expected from the individual polysaccharides(26,27). The interaction with locust bean gum is much stronger and appropriate combinations can form a heat-reversible gel.

Industrially, xanthan gum is used to thicken oil-well drilling muds frequently, where brines are encountered; as a carrier and suspending agent for agricultural sprays and feeds; in the manufacture of gelled and slurry explosives; in gelled or thickened cleaning compositions; in ceramic glazer; and in textile sizing and printing agents. Xanthan gum is also used in formulation of paints and adhesives. For recovery of natural gas, it is used in water based fracturing fluids and in sand-bearing propping agents. In these applications, the polysaccharide can be removed from rock formations by adding a controlled amount of hypochlorite or hydrochloric acid to the fluid before injection into the well(28).

Use of xanthan gum for enhanced oil recovery is being evaluated(29). It represents, by far, the largest potential market for the gum(30). With regard to flow through porous media, pseudoplasticity of xanthan gum at low concentrations imparts desirable low viscosities at the high shear rates encountered during injection but significantly higher viscosities when the waterflood is moving through the formation where there are ultra low shear rates(31). Other advantages attributed to the polysaccharide are high viscosity at low concentrations; resistance to mechanical and chemical degradation: low sensitivity of fluid

properties to pH, elevated temperature, salinity and the presence of divalent metal ions; and low loss from the fluid by retention of the polymer in porous rock[32].

Modified Gum and Its Uses:

Like other polysaccharides, xanthan gum too is susceptible to biodegradation, which limits its application. This limitation has been overcome by modifying the gum[33-37]. One of the technique is grafting, which improves its thermal stability and imparts it with special properties for specific uses Modified gum also finds its application in petroleum industry, food industry, ceramic glazer, textile sizing and printing agents. Dispersions of xanthan gum having high pyruvate content (4 0-4 8%) are much more viscous than dispersions prepared from xanthan gum of low pyruvate content (2.5-3.0%). Grafting monomers on emulsions of xanthan gum in non aqueous liquids gives easily handled dispersions of water soluble or swellable polymer blends[38]

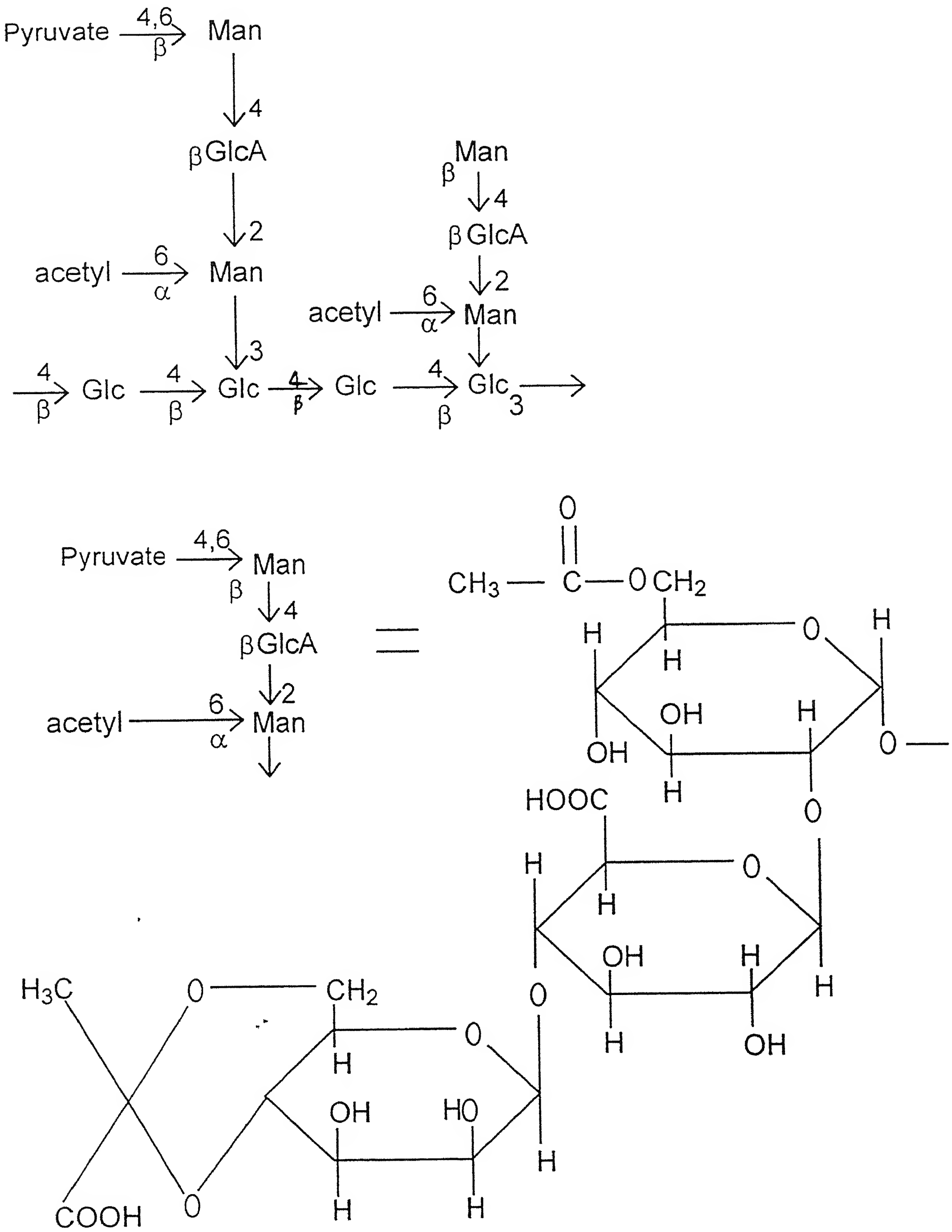

Fig. 2.1 : Structure of Xanthan Gum.

2. GRAFT COPOLYMERIZATION OF ACRYLAMIDE ONTO XANTHAN GUM By Fe^{2+}/BrO_3^- REDOX PAIR:

Modification of natural polymers through graft copolymerization has been the subject of much interest and has paramount contribution towards their improved industrial application. By the process of graft copolymerization, the physical and chemical properties of a synthetic macromolecule are superimposed on the properties of the natural polymer backbone. Graft copolymerization of acrlamide on maize starch by potassium persulphate as initiator shows an increase in the water solubility of the graft copolymer with increase in acrylamide(39). Starch-g-acrylamide when used as retention aids in paper making, increases the bonding between fibres to compensate for the decrease of strength as a result of filler retention(40). Cornstarch-g-acrylamide is useful as flocculant for treating waste water containing Hg^{++} from paper industry(41). When acrylamide is grafted on cellulose its water retention value increases(42). With increase in acrylamide concentration, thermal stability of starch-g-acrylamide is found to increase(43).

The high thickening efficiency hydrogen bonding properties, good electrolytic compatibility and low cost have resulted in xanthan gum being extensively used gum in both food and industrial applications. However it is readily degraded by biological attack which limits its use considerably. To overcome this, it has been grafted with different vinyl monomers employing different initiators. The properties and applications of grafted gum depends upon the type of vinyl monomer grafted.

Polyacrylamide finds extensive application in petroleum industry. It is used in the oil recovery during the drilling process, acidizing of wells and hydraulic fracturing. Polyacrylamide is noted for its application in secondary oil recovery. Studies have shown that graft copolymers of such polysaccharides viz guar gum, carboxymethyl cellulose etc. with acrylamide possesses good drag reducing effectiveness of polyacrylmide and shear stability of polysaccharides(44-47),

accompanied by enhanced thermal stability[48]. Graft copolymer of acrylamide onto cellulose has been used as mercury selective sorbent[49]. Therefore an attempt has been made to prepare xanthan-g-acrylamide graft copolymer with the help of suitable redox pair which is useful in petroleum industry.

Experimental:

Materials:

Acrylamide (E. Merck) was recrystallised twice from methanol and dried in vacuum, ferrous sulphate (AR. BDH), potassium bromate (E. Merck) and xanthan gum (Sigma) were used as such. For hydrogen ion concentration sulphuric acid (E. Merck) of desired concentration was used.

Procedure for Grafting:

For each experiment xanthan gum solution was prepared by adding gum to calculated amount of triple distilled water, so that final volume is 100ml. The reaction was carried out under nitrogen atmosphere at constant temperature. A calculated amount of acrylamide, sulphuric acid and ferrous sulphate solutions were added to the gum solution in the reactor. A known amount of potassium bromate solution was added to initiate the reaction. After a desired interval, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into methanol water mixture[50] while homopolymer remains in the filtrate. The grafted material was dried and weighed.

Homopolymer Content in the Reaction:

To the filtrate a pinch of hydroquinone was added and then it was concentrated by distillation under reduced pressure. The homopolymer was precipitated by pouring the concentrated filtrate into pure methanol. The

homopolymer was separated dried and weighed

RESULT AND DISCUSSION:

The graft copolymer has been characterized according to Fanta's definition(51).

$$\text{Grafting Ratio (\% G)} = \frac{\text{Grafted Polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Grafting Efficiency (\% E)} = \frac{\text{Grafted Polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Add on (\% A)} = \frac{\text{Synthetic Polymer}}{\text{Graft Copolymer}} \times 100$$

$$\text{Conversion (\% C)} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Homopolymer (\% H)} = 100 - \%\text{E}.$$

The effect of variation in concentration of Fe^{2+}, BrO_3^-, hydrogen ion, xanthan gum, acrylamide along with the effect of time and temperature on grafting parameters has been studied.

1. ***Effect of Ferrous ion Concentration:***

The effect of ferrous ion has been studied by varying the concentration of ferrous sulphate from 4.0×10^{-3} to 8.0×10^{-3} mol dm^{-3} (Table 2.1). The grafting ratio, efficiency, add on and conversion increase on increasing the concentration from 4.0×10^{-3} to 8.0×10^{-3} mol dm^{-3} and decrease thereafter with increasing concentration(Fig. 2.2) The increase in grafting ratio with increase in ferrous ion concentration upto the cited range may be attributed to the increase in concentration of the free radicals produced by Fe^{2+}/ BrO_3^- redox pair resulting in the production of xanthan gum radicals at the faster rate.

The decrease in grafting ratio beyond 8.0×10^{-3} mold dm^{-3} may be

attributed to a detrimental factors arising from excess of ferric ions produced by oxidation of ferrous ions. The premature termination of growing grafted chains has been observed by Rogovin et al [52] and Mishra et al.[53] in graft copolymerization initiated with H_2O_2-Fe(II) system beyond certain concentration of Fe(II).

Effect of Bromate Ion Concentration:

The effect of variation in bromate ion concentration has been studied in the range 2.0×10^{-3} to 6.0×10^{-3} moles dm^{-3} (Table 2.2). The grafting ratio, efficiency, add on and conversion decrease with increase in bromate ion concentration(Fig. 2 3). This may be due to the fact that higher concentration of bromate ion favours the formation of homopolymer as is evident by increase in homopolymer with increase in bromate ion concentration.

Effect of Acrylamide Concentration:

The effect of acrylamide concentration on grafting parameters was studied by varying the concentration of acrylamide from 1.0×10^{-2} to 8.0×10^{-2} mol dm^{-3} (Table 2.3). With the increase in concentration of acrylamide upto 4.0×10^{-2} mol dm^{-3}, grafting ratio, efficiency and add on increase and thereafter the values of these parameters decrease with increase in acrylamide concentration(Fig. 2.4). Increase of monomer concentration leads to its accumulation at close proximity of polymer backbone. The monomer molecules which are at the immediate vicinity of reaction sites, become acceptors of xanthan gum macro radical resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules lowering the termination. The decrease in grafting ratio, efficiency and add on with further increase in acrylamide concentration could be interpreted in terms of increase in viscosity of the medium due to the preferential formation of homopolymer at higher concentration.

Effect of Hydrogen IonConcentration:

The effect of hydrogen ion concentration has been studied by varying the

hydrogen ion concentration from $0.9x10^{-3}$ to $5\ 4x10^{-3}$ mol dm^{-3}(Table 2.4). With increase in hydrogen ion concentration, grafting ratio, efficiency, add on and conversion decrease (Fig 2.5) This may be attributed to the fact that high concentration of hydrogen ion favours the conversion of BrO_3^- to Br^- resulting in the decrease of effective concentration of BrO_3^- thereby reducing the production of primary free radicals. Therefore with the increase in hydrogen ion concentration, grafting ratio, efficiency, conversion and add on decrease.

Effect of Xanthan Gum Concentration:

The concentration of xanthan gum has been varied from $50.0x10^{-2}$ to $110x10^{-2}$g dm^{-3} to study the effect of xanthan gum concentration on grafting parameters (Table 2.5). The results reveal that grafting ratio, conversion and add on decrease with increase in gum concentration(Fig. 2.6). This may due to increase in viscosity of the reaction medium with increase in gum concentration which hinders the movement of free radicals, as is evident from the decrease in total conversion of monomer Efficiency, however decreases due to increase in homopolymer formation.

Effect of Time Period:

The effect of time period has been studied by varying the time period from 60 to 180 minutes (Table 2.6). There is increase in grafting ratio, efficiency, conversion and add on with increase in time period, whereas hompolymer decreases with increase in time period(Fig. 2.7). With increase in time period, there is addition of greater number of monomer molecules to the growing grafted chains leading to increase in the values of grafting parameters.

Effect of Temperature:

The effect of temperature on grafting parameters has been studied by

varying the temperature from 30 to 45°C (Table 2.7). Increase in grafting ratio, efficiency, add on and conversion is observed as the temperature is raised from 30 to 35°C, but beyond 35°C these parameters decrease with temperature (Fig. 2.8). Homopolymer, however shows increasing trend with temperature. This trend may be explained on the basis of the fact that with increase in temperature upto the optimum value, the rate of production of primary free radicals increases which increases the grafting sites at greater rate thereby increasing the values of grafting parameters. Beyond optimum value further increase in temperature could result in increase in mobility of macroradicals leading to termination, thereby decreasing the values of grafting parameters. Identical results have been observed in the grafting of acrylamide onto Nylon-6 and silk fibre[54, 55].

EVIDENCE OF GRAFTING:

IR Spectra:

When IR spectra of xanthan gum and xanthan gum-g-acrylamide were compared, the absorption bands corresponding to amide group were observed in the spectra of xanthan gum-g-acrylamide. The band at 1663.44 cm^{-1} is due to overlapping of C=O stretching and N-H bending vibrations. The C-N stretching band of amide group appeared at 1421 cm^{-1}. The frequencies due to N-H stretching vibration and O-H stretching vibration overlapped resulting in the broad band in the region of 2900-3400 cm^{-1}.

Thermal Degradation Behaviour of Xanthan Gum:

The degradation of xanthan gum started at about 232°C, and is a single step degradation reaction. The rate of weight loss increases on increasing the temperature up to 296°C but thereafter it decreases. The char yield of 30%

was obtained at 800°C. Nearly 45% weight loss occured between 200°C and 400°C. Nearly 60% of xanthan gum degraded at 400°C (Table 2.9, Fig.2.16). Therefore final decomposition temperature (FDT) is very low, *i.e.* 316°C. Polymer decomposition temperature (PDT), T_{max} and IPDT of xanthan gum are 281°C, 296°C and 362.8°C respectively (Table 2.8). The linear relationship between Δlog dw/dt vs. Δlog W, where dw/dt is the rate of weight loss and W is residual weight, cannot be obtained. This is because, degradation of xanthan gum is quite complex and starts with depolymerization through random chian scission associated with degradation followed by molecular rearrangements.

Thermal Degradation Behaviour of Xanthan Gum-g-Acrylamide:

Xanthan gum-g-acrylamide graft copolymer has been obtained by grafting acrylamide onto xanthan gum using Fe^{2+}/BrO_3^- redox pair.

The graft copolymer began to degrade at about 175°C. However 5% weight loss has been observed below 120°C, which is attributed to the absorbed water. The degradation appears to be two stage process i.e. from 200 to 360°C and from 360 to 485°C. Rate of weight loss increases on increasing the temperature upto 285°C but thereafter it decreases. The maximum weight loss occured at 285°C (T_{max}). The PDT was found to be 252°C. The final decomposition temperature 444°C is higher than that of xanthan gum. About 40% weight loss occured between 220 to 540°C and 43% char yield was obtained at 800°C. The grafting of acrylamide lowers the initial decomposition temperature of graft copolymer because polyacrylamide chains degrade in the temperature range of 175 to 300°C by the formation of imide group and evolution of ammonia. The IPDT is 294.5°C. (Table 2.8 & Fig. 2.17)

MECHANISM:

Hydroxyl and bromide radicals have been generated in the medium by the interaction of Fe^{2+} and BrO_3^- ions as suggested by Gleason, Mino and Thomas[56].

$$Fe^{2+} + BrO_3^- + H_2O \rightarrow Fe^{3+} + BrO_2^- + OH^{\bullet} + OH^-$$

$$Fe^{2+} + BrO_2^- + H_2O \rightarrow Fe^{3+} + BrO^- + OH^{\bullet} + OH^-$$

$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^- + OH^{\bullet} + OH^-$$

$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^{\bullet} + 2OH^-$$

The hydroxyl and bromide free radicals represented by $R^{\bullet}$, abstracts hydrogen from Xanthan gum molecule producing xanthan gum free radical ($XO^{\bullet}$). The monomer molecules which are in close vicinity of the reaction sites become acceptors of the xanthan gum radicals resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules. In this way grafted chains grow. These grafted chains terminate by coupling to give graft copolymer.

The reaction mechanism can be represented by the following steps.

$$XOH + R^{\bullet} \rightarrow XO^{\bullet} + RH$$

Where $R^{\bullet}$ is hydroxyl ($OH^{\bullet}$) and halogen ($Br^{\bullet}$) free radical.

Initiation:

$$XO^{\bullet} + M \rightarrow XOM_1^{\bullet}$$

$$R^{\bullet} + M \rightarrow RM_1^{\bullet}$$

Propagation:

$$XOM_1^{\bullet} + M \rightarrow XOM_2^{\bullet}$$

$$XOM_2^{\bullet} + M \rightarrow XOM_3^{\bullet}$$

... .

$$XOM_{n-1}^{\bullet} + M \rightarrow XOM_n^{\bullet}$$

$$RM_1^{\bullet} + M \rightarrow RM_2^{\bullet}$$

$$RM_2^{\bullet} + M \rightarrow RM_3^{\bullet}$$

. . ..

.. . .

. . . .

$$RM_{n-1}^{\bullet} + M \rightarrow RM_n^{\bullet}$$

Termination :

$$XOM_n^{\bullet} + XOM_m^{\bullet} \rightarrow \text{graft copolymer}$$

$$XOM_n^{\bullet} + RM_n^{\bullet} \rightarrow \text{graft copolyme}$$

$$RM_n^{\bullet} + RM_m^{\bullet} \rightarrow \text{homopolymer}$$

See References On Page No. 58-63

Table 2.1

Effect of Ferrous Ion

$[BrO_3^-]$ = 4.0 x 10^{-3} mol dm^{-3}, [ACM] = 4.0 x 10^{-2} mol dm^{-3}; $[H^+]$ = 1.8x10^{-3} mol dm^{-3}; [Xanthan Gum] = 65.0x10^{-2} g dm^{-3}; Time = 120 min; Temp = 35°C.

S N.	$[Fe^{2+}]$x10^3 mol dm^{-3}	% G	% A	% C	% E	% H
1.	4.0	110 9	52.5	35.1	72.2	27.8
2.	5 0	129.1	56.3	37.8	78.0	22.0
3.	6.0	104.8	51.2	32.3	74.2	25.8
4	7 0	86.8	46 5	28 1	70.6	29.4
5	8 0	72.5	42.0	25 3	65.5	34.5

Table 2.2

Effect of Bromate Ion

$[Fe^{2+}]$ = 5.0x10^{-3} mol dm^{-3}; $[H^+]$ = 1.8x10^{-3} mol dm^{-3} [ACM] = 4.0x10^{-2} mol dm^{-3}; [Xanthan Gum] = 65.0 x 10^{-2} g dm^{-3} Time = 120 min.; Temp =35°C

S.N.	$[BrO_3^-]$x10^3 mol dm^{-3}	% G	% A	% C	% E	% H
1	2.0	145.6	59 0	39.2	84.9	15.1
2	3.0	132.7	57.0	38.4	79.0	21.0
3.	4.0	129.1	56.3	37.8	78.0	22.0
4.	5.0	118.2	54.2	36.4	74.2	25.8
5.	6.0	83.4	45.5	32.4	58.8	41.1

Table 2.3

Effect of Acrylamide

$[Fe^{2+}]$ = 5.0x10^{-3} mol dm^{-3}; $[BrO_3^-]$ = 4.0x10^{-3} mol dm^{-3}
$[H^+]$ = 1.8x10^{-3} mol dm^{-3}; [Xanthan Gum] = 65.0 x 10^{-2} g dm^{-3}
Time = 120 min.; Temp =35°C

S.N.	[ACM]x10^2 mol dm^{-3}	% G	% A	% C	% E	% H
1.	1.0	50.2	33 4	63.6	72.1	27.9
2.	2.0	81.5	44 9	49.5	75.2	24.8
3.	4.0	129.1	56 3	37 8	78.0	22.0
4.	6.0	108.4	51.9	23.5	70.2	29.8
5	8.0	101.2	50.2	17.6	65.5	34.5

Table 2.4

Effect of Hydrogen Ion

$[Fe^{2+}]$ = 5.0x10^{-3} mol dm^{-3}; $[BrO_3^-]$= 4x10^{-3} mol dm^{-3};
[ACM] = 4.0x10^{-2} mol dm^{-3}; [Xanthan Gum] = 65.0 x 10^{-2} g dm^{-3}
Time = 120 min.; Temp =35°C

S.N.	$[H^+]$ x 10^3 mol dm^{-3}	% G	% A	% C	% E	% H
1	0.9	242.3	70.7	57.2	96.8	3.2
2.	1.8	129 1	56.3	37.8	78.0	22.0
3.	2.7	112.3	52.8	38.1	67.5	32.5
4.	3 6	84.1	45.6	32.4	59.3	40.7
5.	5 4	49.7	33.2	22.2	51.0	49.0

See References On Page No. 58-63

Table 2.5

Effect of Xanthan Gum

$[Fe^{2+}] = 5.0x10^{-3}$ mol dm^{-3}; $[BrO_3^-]= 4x10^{-3}$ mol dm^{-3}; [ACM] = $4.0x10^{-2}$ mol dm^{-3}; $[H^+] = 1.8x\ 10^{-3}$ mol dm^{-3} Time = 120 min.; Temp =35°C

S N.	[Gum] x 10^2 g dm^{-3}	% G	% A	% C	% E	% H
1	50 0	190.2	65.5	44 5	75.2	24.8
2.	65 0	129.1	56.3	37.8	78.0	22.0
3.	80 0	86.3	46.3	28.3	85.6	14.4
4.	95.0	78 5	43 9	28 4	92.2	7.8
5.	110.0	61 3	38.0	25.4	93.3	6.7

Table 2.6

Effect of Time Period

$[Fe^{2+}] = 5.0x10^{-3}$ mol dm^{-3}; $[BrO_3^-]= 4x10^{-3}$ mol dm^{-3}; [ACM] = $4.0x10^{-2}$ mol dm^{-3}; [Xanthan Gum] = 65.0 x 10^{-2} g dm^{-3}; $[H^+] = 1.8x10^{-3}$ mol dm^{-3}; Temp =35°C

S N.	Time Period (Min)	% G	% A	% C	% E	% H
1	60	112.2	52.8	35.3	72.6	27.4
2.	90	122.1	54.4	37.2	75.3	24.7
3.	120	129.1	56.3	37.8	78.0	22.0
4.	150	140.2	58.4	40.2	79.7	20.3
5	180	150.1	60.0	42.5	80.7	19.3

See References On Page No. 58-63

Table 2.7

Effect of Temperature

$[Fe^{2+}]$ = 5.0x10^{-3} mol dm^{-3}; $[BrO_3^-]$= 4x10^{-3} mol dm^{-3};
[ACM] = 4.0x10^{-2} mol dm^{-3}; $[H^+]$ = 1.8x 10^{-3} mol dm^{-3};
[Xanthan Gum] = 65.0 x 10^{-2} g dm^{-3}; Time = 120 min.;

S.N.	Temp °C	% G	% A	% C	% E	% H
1.	30	104.8	51.1	31.8	75.2	24.8
2.	35	129.1	56.3	37.8	78.0	22.0
3.	40	101.2	50.2	31.8	74.2	25.8
4.	45	92.3	47.9	29.9	70.4	29.6

Table 2.8

THERMOGRAVIMETRIC ANALYSIS OF GRAFT COPOLYMER

Sample Code	**PDT (°C)**	**FDT (°C)**	**T_{max} (°C)**	**IPDT (°C)**
G_1	281.0	316.0	296.0	362.8
G_2	252.0	444.0	285.0	294.5

Table 2.9

DECOMPOSITION TEMPERATURE (T°D)

Sample	**T°D (°C) at following weight loss**						
	10%	**20%**	**30%**	**40%**	**50%**	**60%**	**70%**
G_1	270.0	282.0	297.0	310.0	343.0	527.0	790.0
G_2	220.0	280.0	320.0	390.0	540.0	850.0	--

Table 2.10

DECOMPOSITION TEMPERATURE (T°D)

Temp (°C)	Weight loss (%)	
	G_1	G_2
100	3.3	2.8
200	6.0	8.3
300	29.0	27.0
400	45.0	41.0
500	49.0	49.0
600	52.0	52.0
700	54.0	54.0
800	58.0	58.0

G_1 = Xanthan gum

G_2 = Xanthan gum-g-acrylamide (Fe^{2+}/BrO_3^-)

See References On Page No. 58-63

3. GRAFT COPOLYMERIZATION OF ACRYLEC ACID ONTO XANTHAN GUM BY POTASSIUM MONOPERSULPHATE (PMS)/Fe^{2+} REDOX PAIR:

Grafting provides a convenient method for tailoring material properties to specific end uses Grafting of polyacrylic acid onto xanthan gum has been studied with the objective of improving or modifying the properties of xanthan gum in an attempt to develop new materials by combining the properties of both natural and synthetic polymer.

Acrylic acid possesses some unique characteristics. Therefore polymers derived from it may find many commercial applications. One of the earliest fields of application of polyacrylic acid was in thickening. Thickening action in water may be used in secondary recovery of petroleum in oil fields, tooth pastes, cosmetics, hydraulic fluids and even liquid rocket-fuels have been thickened or gelled using acrylic acid polymers(57). Cross linked acrylic acid polymer provide useful ion exchange resins where weak acids are desired instead of strong sulfonic acid types. Recovery of antibiotic and sugar manufacture are among the many areas where this is desirable. Polycrylic acid is used as suspending agents and despersants in drilling mud additive for oil wells, paints and in cements. Long chain linear polymers of acrylic acid can be used to aggregate suspended particles in areas such as treatment of both potable and waste water, recovery of suspended metal ores in mining operations and clarification of sugar cane juice. Polymers of acrylic acid can be formulated to impart green strength to molded articles such as ceramics or foundry core binders.

Graft copolymerization of acrylic acid has been studied on various synthetic and natural polymeric substrate(58-60). Melt grafting of acrylic acid onto isolactic polypropylene resulted in the improvement of thermo chemical properties and β phase formation of graft copolymer(61). Graft copolymer of

acrylic acid onto maize starch using $K_2S_2O_8$ as free radical initiator were prepared under different conditions(62). Acrylic acid graft copolymer showed, marked improvement in the water retention capacity(63, 64). Hebeish and coworkers(65) have reported polyacrylic acid starch composite as a substitute for sodium alginate in printing cotton fabrics with reactive dyes. Graft copolymerization of acrylic acid onto starch has been carried out at different conditions with $(NH_4)_2S_2O_8$ as a catalyst(66). It has been found that fabric samples sized with graft copolymer acquire break and abrasion resistance than that sized with native rice starch(67). Lignin-grafted acrylic copolymers are very good absorbents and are used as water retention agents for soils(68). Thus it is evident that polyacrylic acid has wide range of applications in various fields. Xanthan gum also enjoys a wide range of usage in industrial applications such as paper, mining and textile industry and in oil wells etc. Thus it was thought worthwhile to graft acrylic acid onto xanthan gum so as to produce a graft copolymer which is better flocculating and sizing agent than pure xanthan gum. The graft copolymer will find various new application such as ion exchange resin, desiccants etc.

EXPERIMENTAL:

Materials:

Acrylic acid (Aldrich) was freshly distilled over copper turnings under vacuum and the middle fraction was used. Xanthan gum (Sigma), potassium monopersulphate (Du Pont Co USA) and ferrous sulphate (AR BDH) were used as such. Sulphuric acid (E.Merck) was used for maintaining hydrogen ion concentration.

Procedure for Graft Copolymerization:

Xanthan gum solution was prepared by slow addition of weighed amount of gum to calculated amount of triple distilled water in a reactor, so

that final volume is 100 ml. Calculated amounts of potassium monopersulphate(PMS), H_2SO_4 and acrylic acid were added to the reactor and nitrogen was allowed to pass through the mixture as well as ferrous Sulphate solution. After half an hour calculated amount of ferrous sulphate solution was added to the reactor to initiate the reaction and the reaction was to allowed to run for desired interval of time at constant temperature. After the desired interval of time, the reaction was stopped by letting air in the reactor. The reaction mixture was poured in a water-methanol mixture. The grafted gum separates out which was filtered dried and weighed. There was no formation of homopolymer polyacrylic acid.

RESULT AND DISCUSSION:

The graft copolymer has seen characterized according to Fanta`s definition as discussed earlier. The effect of variation in concentration Fe^{2+}, hydrogen ion, xanthan gum, acrylic acid and potassium monopersulphate along with the effect of time period and temperature on grafting parameter has been studied.

Effect of Ferrous concentration:

The effect Fe^{2+} concentration has been studied by varying the concentration from 2.0x10^{-3} to 8.0x10^{-3} mol dm^{-3} (Table 2.11). There is an increase in grafting ratio add on and conversion as the concentration is increased from 2.0x10^{-3} to 5.0x10^{-3} mol dm^{-3} beyond this concentration, the values of these parameters decrease (Fig. 2.9).

The increase in the values of grafting parameters up to the cited concentration could be due to the increased production of free radicals by the PMS Fe^{2+} redox pair resulting in the production of xanthan gum radicals at the faster rate.

The decrease in grafting ratio beyond 5.0x10^{-3}mol dm^{-3} may be attributed to a detrimental factor arising from excess of Fe(III) ions produced by oxidation

of Fe(II). The premature termination of growing grafted. Chains has been observed by Rogovin et al. [69] and Mishra et al. [70] in graft copolymerization on initiated with H_2O_2/Fe^{2+} system beyond certain concentration of Fe^{2+}.

Effect of Potassium monopersulphate concentration

It has been observed that grafting ratio, add on and conversion increase on increasing the concentration of PMS from $1.0x10^{-3}$ to $4.0x10^{-3}$ mol dm $^{-3}$, but beyond this concentration the values of these parameters decrease with increase in PMS concentration (Table-2.12, Fig. 2.10). The enhancement of grafting within the cited range may be attributed to the progressive reduction producing hydroxyl free radicals and sulphate ion radicals which attack the gum molecule creating more free radical sites to which monomer addition takes place. After cited concentration of PMS, the decrease in grafting may be due to the premature temination of growing grafted chais by the hydroxyl free radical or sulphate ion free radical produced in excess at higher PMS concentration.

Effect of Acrylic Acid concentration:

The effect of monomer concentration on grafting reaction has been studied at various concentration of acrylic acid (Table-2.13). With increase in acrylic acid concentration ($2.0x10^{-2}$ to $5.0x10^{-2}$ mol dm^{-3}) grafting ratio add on and conversion increase. Thereafter the values of these parameters decrease (Fig. 2.11). This observation due to the fact that acrylic acid exhibits gelation and due to gelation, the movement of growing polymeric chains is restricted lowering the termination, resulting in the increase in grafting ratio. The decrease in the values of the grafting parameters beyond the cited range may be due to increase in viscosity of the reaction medium resulting in the restricted movement of free radicals.

Effect of Hydrogen Ion Concentration:

The concentration of hydrogen ion plays an important role in graft copolymerization. The graft copolymerization could not be effected in neutral or

alkaline medium because of immediate precipitation of iron hydroxide. Grafting ratio, add on and conversion decrease on increasing the hydrogen ion concentration (Table-2.14, Fig 2.12). This behaviour may be explained on the basis of the fact that with increase in hydrogen in concentration the concentration of species HSO_5^- decreases resulting in the less production of primary free radicals thereby decreasing the grafting parameters.

Effect of Xanthan gum Concentration:

The effect of change in xanthan gum concentration on grafting parameters has been summarized in Table (2.15). Grafting ratio, add on and conversion increase on increasing the gum concentration from 0.60 to 1.000 g dm^{-3}, thereafter the value of these parameters decrease (Fig. 2.13). The increase in grafting ratio up to the cited concentration of gum may be due to availability of more grafting sites with increase in concentration, but beyond the cited range viscosity of the reaction medium increases which hinders the movement of free radical thereby decreasing the value of grafting parameters.

Effect of Time Period:

The effect of change in duration of grafting reaction was studied by varying the time period from 60 to 180 min. (Table-2.16). Grafting ratio, add on and conversion increase with increase in time period (Fig. 2.14). The increase in grafting parameters may be attributed to the addition of more and more monomer molecules to the growing grafted chains as the duration of reaction is increased.

Effect of Temperature:

The effect of temperature on grafting parameters has been summarised in Table-2.17. It has been observed that as the temperature is increased (25 to 35^0) grafting ratio, add on and conversion increase but beyond $35^{\circ}C$ the decrease in the values of these parameters has been observed (Fig. 2.15). The increase in the grafting ratio add on and conversion up to cited range may be attributed to the fact that, with increase in temperature, rate of production of primary free radicals

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increases which generates the grafting sites at greater rate, thereby increasing the values of grafting parameters. However, beyond the optimum value further increase in temperature could result in increase in mobility of macro radicals leading to termination there by decreasing the values of the grafting parameters.

Thermal Degradation Behaviour of Xanthan Gum-g-Acrylic Acid:

Xanthan gum-g-acrylic acid graft copolymer has been obtained by grafting acrylic acid onto xanthan gum using PMS/Fe^{2+} redox pair.

The graft copolymer began to degrade at about 200°C. However 5% weight loss has been observed below 100°C. Which may be attributed to the absorbed water The degradation appears to be three-stage process i.e. from 236.9 to 337 1°C, from 337.1 to 436.5°C and from 436.5 to 761.6°C. The maximum weight loss occured at 436.5°C (T_{max}). The polymer decomposition temperature (PDT) was found to be 236.9°C. The final decomposition temperature (FDT) was found to be 761.6°C, which is higher than that of xanthan gum. About 55% weight loss occured between 100 and 760°C and 33% char yield was obtained at 766°C. The IPDT was found to be 294.5°C (Table 2.18 & Fig. 2.18).

MECHANISM:

$OH^{\circ}$and $SO_4^{-\circ}$ radicals are generated by the interaction of Fe^{2+} and $KHSO_5$. The OH° and $SO_4^{-\circ}$ radicals represented by R° abstracts hydrogen atom from xanthan gum molecule producing xanthan gum radical (XO°). The monomer molecules which are in close vicinity of the reaction sites become acceptors of the xanthan gum radicals resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules. In this way, grafted chains grow. These grafted chains terminate by coupling to give graft copolymer.

The following steps can represent the reaction mechanism:

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + OH^- + SO_4^{-\bullet}$$

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + OH^\bullet + SO_4^{2-}$$

$$XOH + R^\bullet \rightarrow XO^\bullet + RH$$

$$(R^\bullet = OH^\bullet, SO_4^{-\bullet})$$

Initiation:

$$XO^\bullet + M \rightarrow XOM^\bullet_1$$

Propagation:

$$XOM_1^\bullet + M \rightarrow XOM_2^\bullet$$

$$XOM_2^\bullet + M \rightarrow XOM_3^\bullet$$

.. ..

....

....

$$XOM_{n-1}^\bullet + M \rightarrow XOM_n^\bullet$$

Termination:

$$XOM^\bullet_n + XOM^\bullet_m \rightarrow \text{graft copolymer}$$

See References On Page No. 58-63

Table 2.11

Effect of Ferrous Ions

[PMS] = 4.0 x 10^{-3} mol dm^{-3}, [AA] = 5.0 x 10^{-2} mol dm^{-3}; [H^+] = 1.8x10^{-3} mol dm^{-3}; [Xantham Gum] = 1.0x10^{-2} g dm^{-3}; Time = 120 min; Temp = 35°C.

S N.	[Fe^{2+}]x10^3 mol dm^{-3}	% G	% A	% C
1	2.0	31.9	24 2	9.1
2	3.5	101.4	50.3	29.0
3.	5 0	192.3	65.8	54.9
4.	6.5	183.3	64.6	52.4
5.	8 0	172 7	63.3	49.3

Table 2.12

Effect of PMS

[Fe^{2+}] = 5.0x10^{-3} mol dm^{-3}; [H^+] = 1.8x10^{-3} mol dm^{-3} [AA] = 5.0x10^{-2} mol dm^{-3}; [Xantham Gum] = 1.0 g dm^{-3} Time = 120 min.; Temp =35°C

S.N.	[PMS]x10^3 mol dm^{-3}	% G	% A	% C
1.	1 0	135 9	57.6	38.8
2.	2.5	154.3	60.6	44.0
3.	4.0	192.3	65.8	54.9
4.	5.5	181.4	64.5	51.8
5.	7.0	171.5	63.2	49.0

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Table 2.13

Effect of Acrylic acid

[PMS] = 4.0x10^{3-}; [Fe^{2+}] = 5.0x10^{-3} mol dm^{-3};
[H^+] = 1.8x10^{-3} mol dm^{-3}; [Xantham Gum] =1.0 g dm^{-3}
Time = 120 min.; Temp =35°C

S N	[AA]x10^{2} mol dm^{-3}	% G	% A	% C
1.	2.0	78.3	43.9	22.4
2.	3.5	107.2	51.7	42.5
3.	5.0	192 3	65.8	54.9
4.	6.5	111.0	52.6	23.7
5	8.0	103.2	50.7	17.9

Table 2.14

Effect of Hydrogen Ion

[PMS] = 4.0x10^{-3}; [Fe^{2+}] = 5.0x10^{-3} mol dm^{-3};
[AA] = 5.0x10^{-2} mol dm^{-3}; [Xantham Gum] = 1.0 g dm^{-3}
Time = 120 min.; Temp =35°C

S.N.	[H^+]x10^{3} mol dm^{-3}	% G	% A	% C
1.	0.9	230.4	69.4	65.8
2.	1.35	212.3	67.9	60.7
3.	1.80	192.3	65.8	54.9
4.	2.25	145 3	59.2	41.5
5.	2.70	113.4	53.1	32.4

See References On Page No. 58-63

Table 2.15

Effect of Xanthan Gum

**[PMS] = $4.0x10^{-3}$; [Fe^{2+}] = $5.0x10^{-3}$ mol dm^{-3};
[AA] = $5.0x10^{-2}$ mol dm^{-3}; [H^{+}] = 1.8x 10^{-3} mol dm^{-3};
Time = 120 min.; Temp =35°C**

S.N	[Gum] g dm^{-3}	% G	% A	% C
1	0.6	129 1	56.3	22.1
2.	0 80	139.2	58.2	31.8
3	1 00	192.3	65.8	54.9
4.	120	152.3	60.4	52.2
5.	1.40	135.2	57 5	54.1

Table 2.16

Effect of Time Period

**[Fe^{2+}] = $5.0x10^{-3}$ mol dm^{-3}; [PMS] = $4.0x10^{-3}$ mol dm^{-3};
[H^{+}] = $1.8x10^{-3}$ mol dm^{-3}; [AA] = $5.0x10^{-2}$ mol dm^{-3};
[Xantham Gum] = 1.0 g dm^{-3}; Temp =35°C**

S.N	Time (Min)	% G	% A	% C
1.	60	139.5	58.2	39.8
2.	90	156.6	61.8	44.7
3.	120	192.3	65.8	54.9
4.	150	212.3	67.9	60.6
5.	180	255.3	71.8	72 9

Table 2.17

Effect of Temperature

[PMS] = 4.0x10^{-3} mol dm^{-3}; [Fe^{2+}] = 5.0x10^{-3} mol dm^{-3}; [H^+] = 1.8x 10^{-3} mol dm^{-3}; [AA] = 5.0x10^{-2} mol dm^{-3}; [Xantham Gum] = 1.0 g dm^{-3}; Time = 120 min.;

S N	Temp (°C)	% G	% A	% C
1.	25	131.4	56.7	37.5
2.	30	144.6	59 1	41.3
3	35	192.3	65.8	54.9
4	40	169.3	62.8	48.4
5.	45	112.6	52.9	32.2

Table 2.18

THERMOGRAVIMETRIC ANALYSIS OF GRAFT COPOLYMER

Sample Code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
G_1	281.0	316.0	296.0	362.8
G_2	236.9	761.6	436.5	294.5

Table 2.19

DECOMPOSITION TEMPERATURE (T°D)

Sample	T°D (°C) at following weight loss						
	10%	20%	30%	40%	50%	60%	70%
G_1	270.0	282.0	297.0	310.0	343.0	527.0	790.0
G_2	124 0	229.0	295.0	376.0	437.0	633.0	850.0

See References On Page No. 58-63

Table 2.20

DECOMPOSITION TEMPERATURE (T°D)

Temp (°C)	Weight loss (%)	
	G_1	G_2
100	3.3	7.0
200	6.0	15.4
300	29.0	32.3
400	45.0	44.0
500	49.0	59.0
600	52.0	62.3
700	54.0	65.0
800	58.0	72.0

G_1 = Xanthan Gum

G_2 = Xanthan Gum-g-acrylic acid (PMS/Fe^{2+})

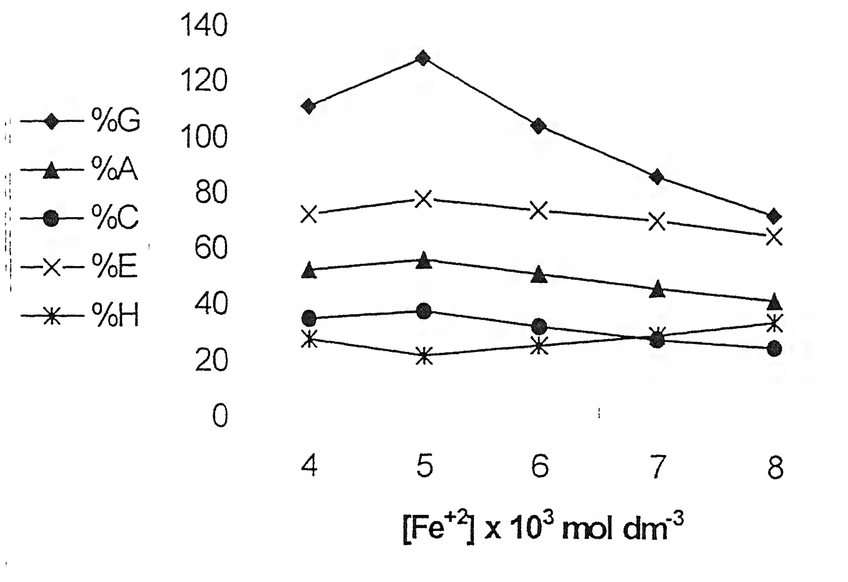


Figure 2.2 $[BrO_3^-] = 4.0\times10^{-3}$ mol dm^{-3}; [ACM] = 4.0×10^{-2} mol dm^{-3}; $[H^+] = 1.8\times10^{-3}$ mol dm^{-3}, [XOH]=65.0×10^{-2} g dm^{-3}, Time 120 min.; Temp. 35°C

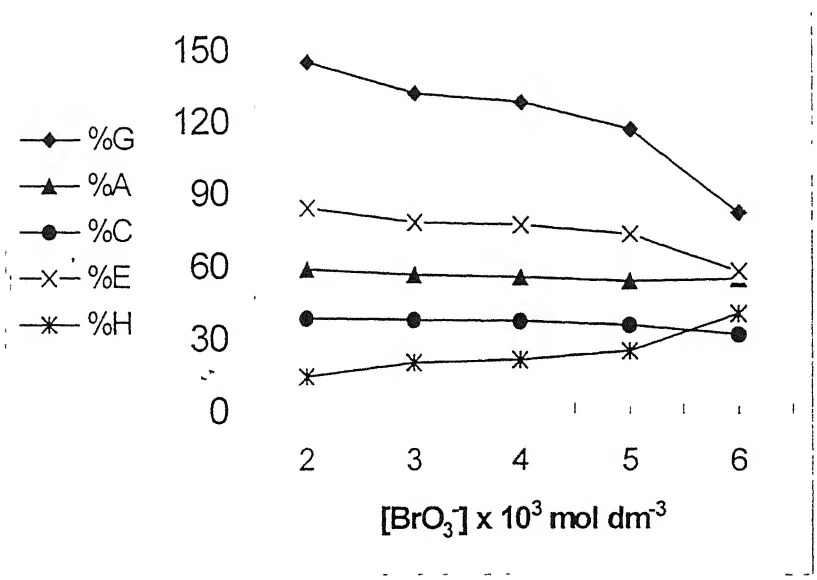


Figure 2.3 $[Fe^{2+}] = 5.0\times10^{-3}$ mol dm^{-3}; [ACM] = 4.0×10^{-2} mol dm^{-3}; $[H^+] = 1.8\times10^{-3}$ mol dm^{-3}; [XOH]=65.0×10^{-2} g dm^{-3}; Time 120 min.; Temp. 35°C

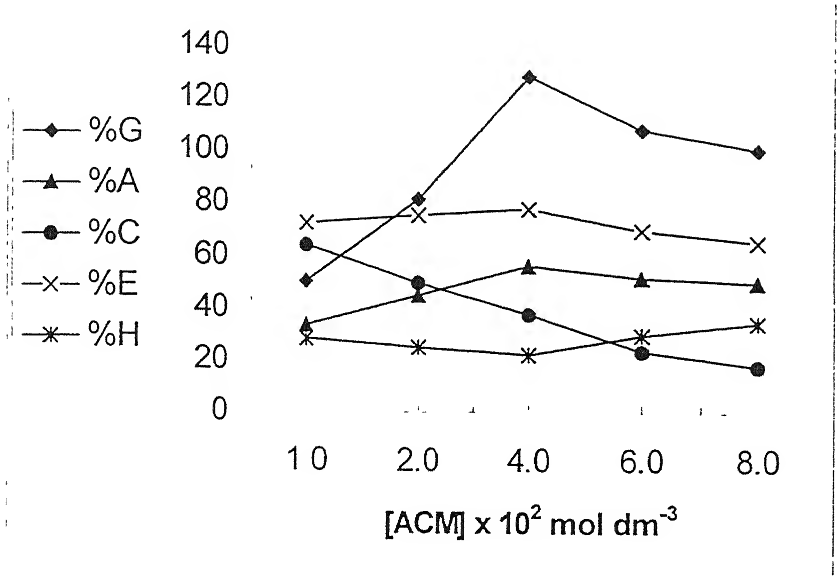


Figure 2 4 $[Fe^{2+}] = 5.0\times10^{-3}$ mol dm^{-3}, $[BrO_3^-] = 4.0\times10^{-3}$ mol dm^{-3}; $[H^+] = 1.8\times10^{-3}$ mol dm^{-3}; [XOH]=65.0×10^{-2} g dm^{-3}; Time 120 min.; Temp. 35°C

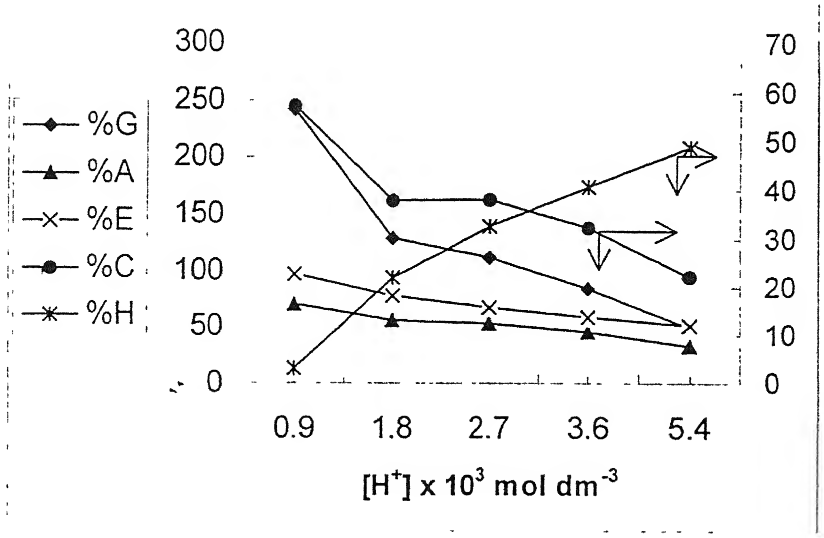


Figure 2.5 $[Fe^{2+}] = 5.0\times10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0\times10^{-3}$ mol dm^{-3}; [ACM] = 4.0×10^{-2} mol dm^{-3}; [XOH]=65.0×10^{-2} g dm^{-3}; Time 120 min.; Temp. 35°C

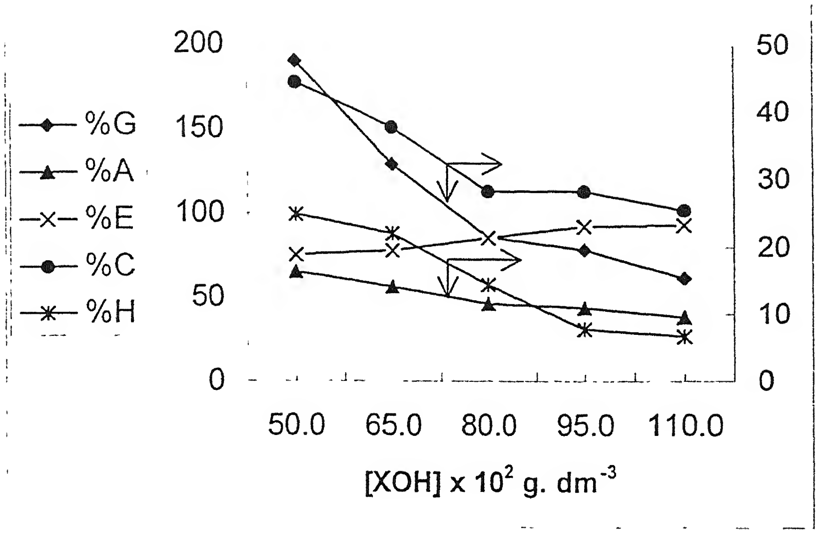


Figure 2.6 $[Fe^{2+}] = 5.0\times10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0\times10^{-3}$ mol dm^{-3}; [ACM] = 4.0×10^{-2} mol dm^{-3}, $[H^+]=1.8\times10^{-3}$ mol dm^{-3}; Time 120 min.; Temp. 35°C

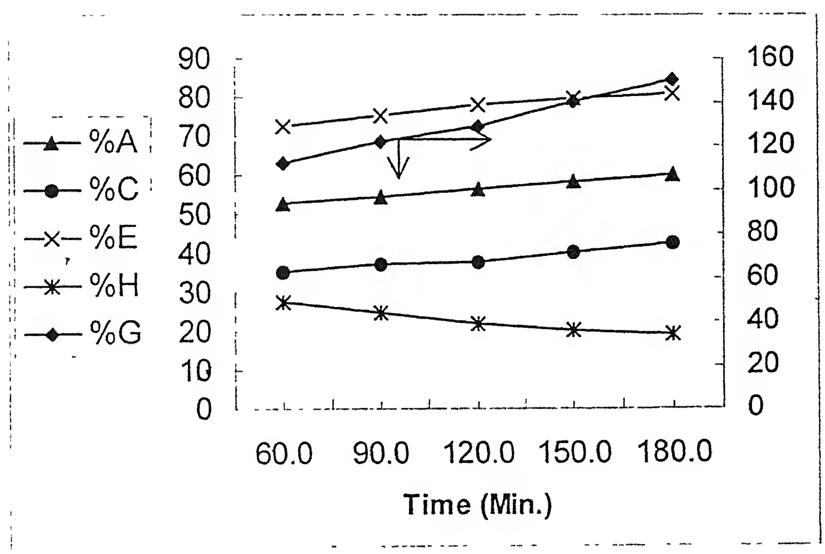


Figure 2.7 $[Fe^{2+}] = 5.0\times10^{-3}$ mol dm^{-3}; $[BrO_3^-] = 4.0\times10^{-3}$ mol dm^{-3}; [ACM] = 4.0×10^{-2} mol dm^{-3}; $[H^+]=1.8\times10^{-3}$ mol dm^{-3}; [XOH]=65.0×10^{-2} g. dm^{-3}; Temp. 35°C

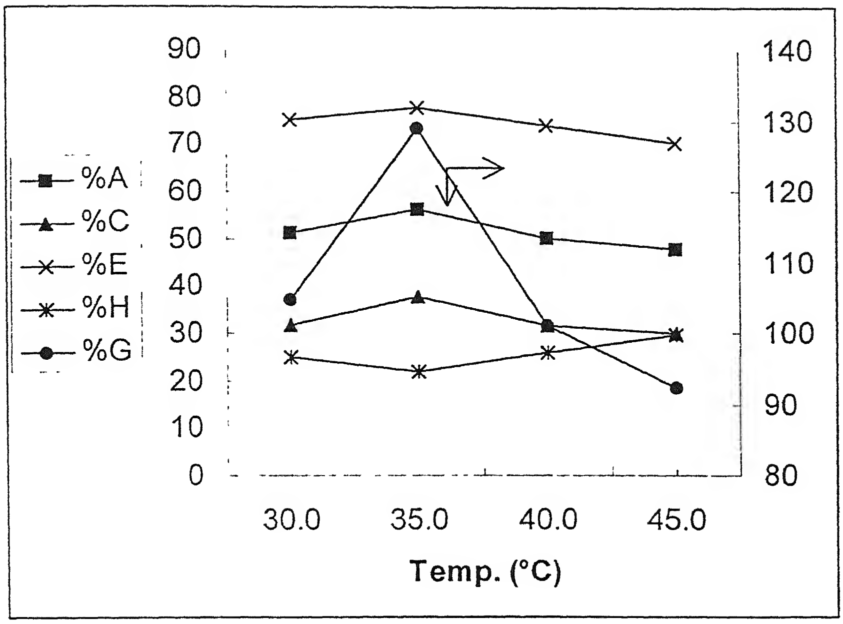


Figure 2.8 $[Fe^{2+}]= 5.0 \times 10^{-3}$ mol dm^{-3}; $[BrO_3^-]= 4.0\times10^{-3}$ mol dm^{-3}; [ACM]= 4.0×10^{-2} mol dm^{-3}; $[H^+]= 1.8\times10^{-3}$ mol dm^{-3} ; [XOH]= 65.0×10^{-2} g. dm^{-3}; Time = 120 min.

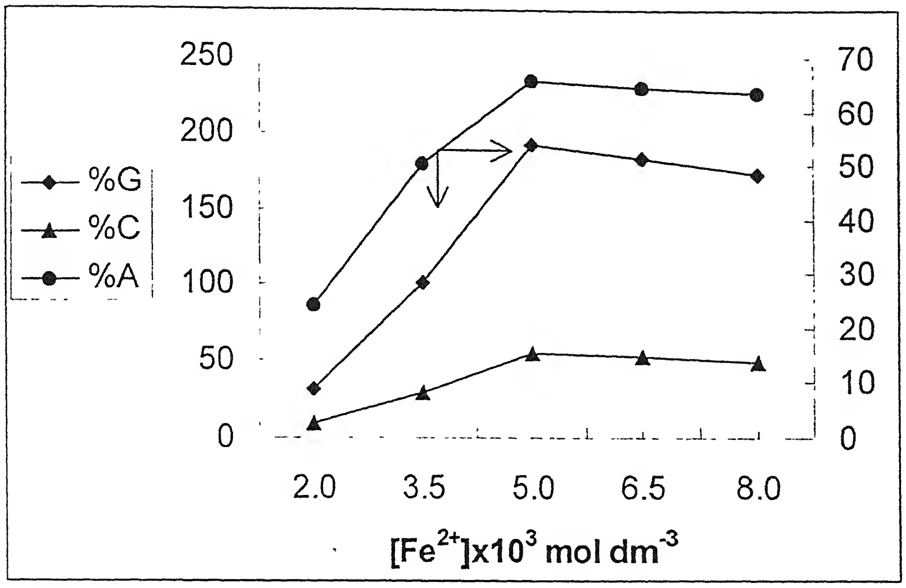


Figure 2.9 [PMS]= 4.0 $\times 10^{-3}$ mol dm^{-3}; [H^+]= 1.8 $\times$ 10^{-3} mol dm^{-3}; [AA]= 5.0 $\times 10^{-2}$ mol dm^{-3}; [XOH]= 1.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

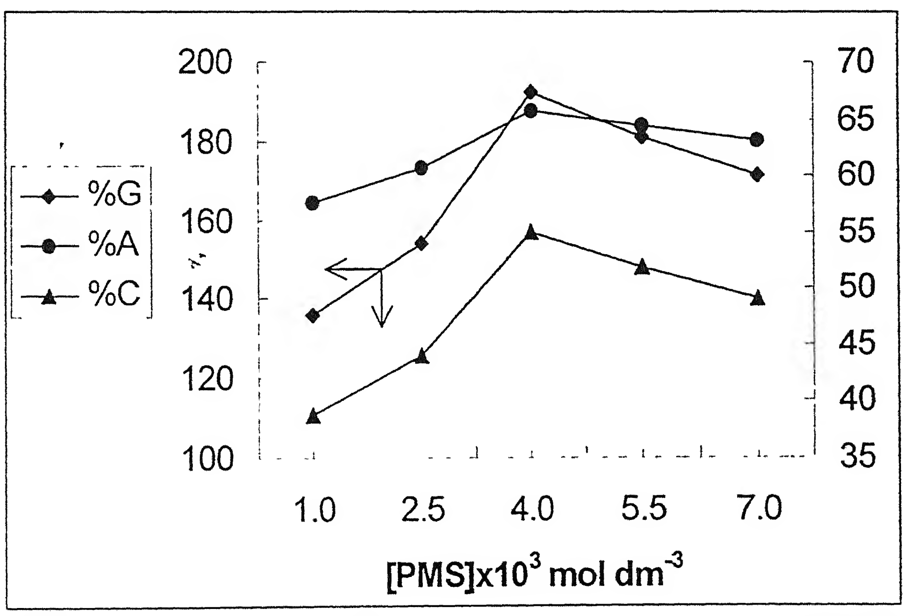


Figure 2.10 [Fe^{2+}]= 5.0 $\times 10^{-3}$ mol dm^{-3}; [H^+]= 1.8 $\times$ 10^{-3} mol dm^{-3}; [AA]= 5.0 $\times 10^{-2}$ mol dm^{-3}; [XOH]= 1.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

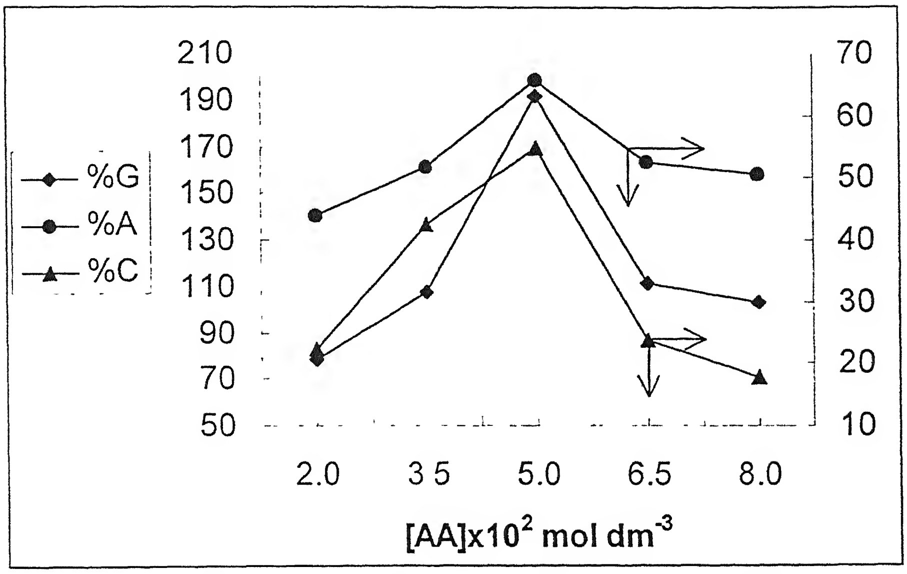


Figure 2.11 $[Fe^{2+}]$= 5.0 ×10^{-3} mol dm^{-3}; $[H^+]$= 1.8 × 10^{-3} mol dm^{-3}; [PMS]= 4.0 ×10^{-3} mol dm^{-3}; [XOH]= 1.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

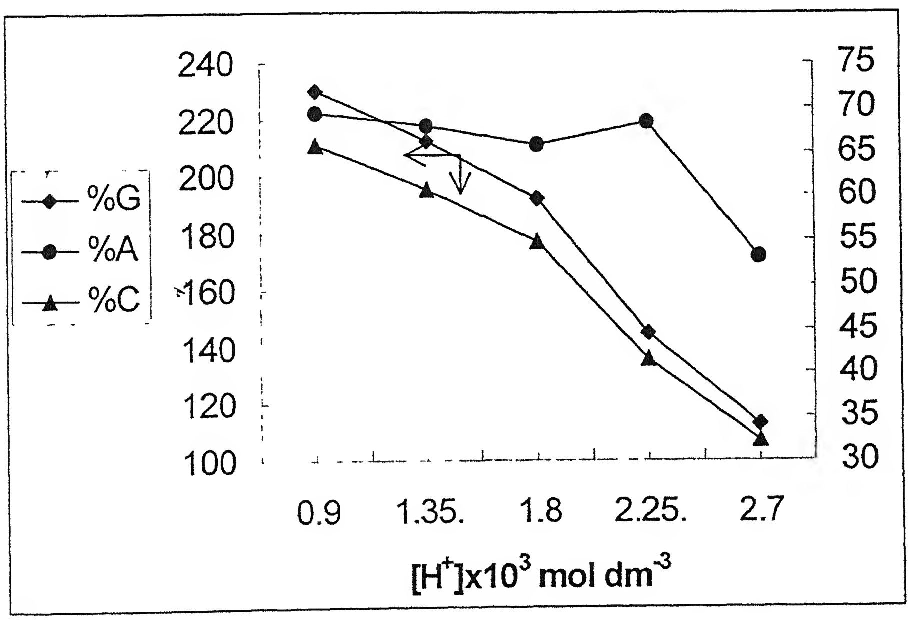


Figure 2.12 $[Fe^{2+}]$= 5.0 ×10^{-3} mol dm^{-3}; [AA]= 5.0 × 10^{-2} mol dm^{-3}; [PMS]= 4.0 ×10^{-3} mol dm^{-3}; [XOH]= 1.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

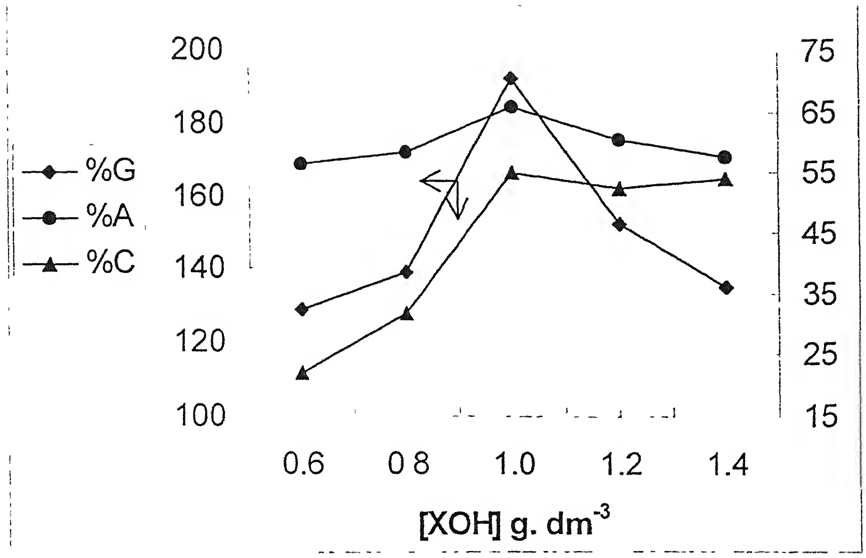


Figure 2 13 $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; [AA] $= 5.0 \times 10^{-2}$ mol dm^{-3}; [PMS] $= 4.0 \times 10^{-3}$ mol dm^{-3}; $[H^{+}] = 1.8 \times 10^{-3}$ mol dm^{-3}; Time = 120 min. ; Temp.= 35°C.

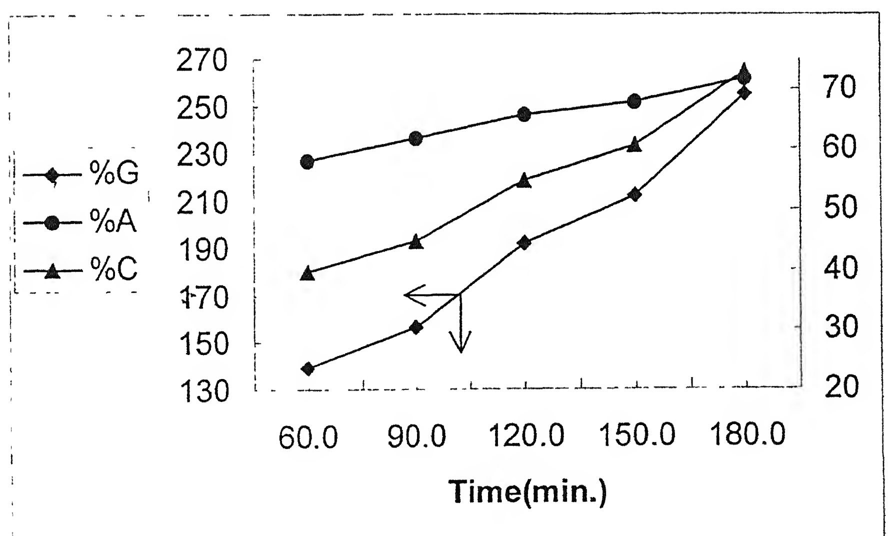


Figure 2 14 $[Fe^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3}; [AA] $= 5.0 \times 10^{-2}$ mol dm^{-3}; [PMS] $= 4.0 \times 10^{-3}$ mol dm^{-3}; $[H^{+}] = 1.8 \times 10^{-3}$ mol dm^{-3}; [XOH]= 1.0 g. dm^{-3}; Temp.= 35°C.

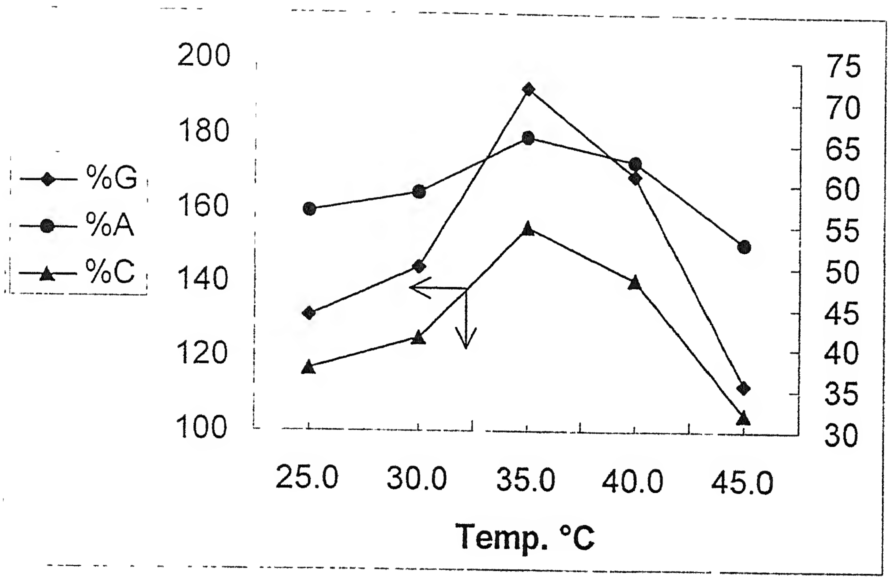


Figure 2.15 $[Fe^{2+}]$= 5.0 ×10^{-3} mol dm^{-3}; [AA] = 5.0 × 10^{-2} mol dm^{-3}; [PMS] = 4.0 ×10^{-3} mol dm^{-3}; $[H^+]$ = 1.8×10^{-3} mol dm^{-3}; [XOH]= 1.0 g. dm^{-3}; Time= 120 min..

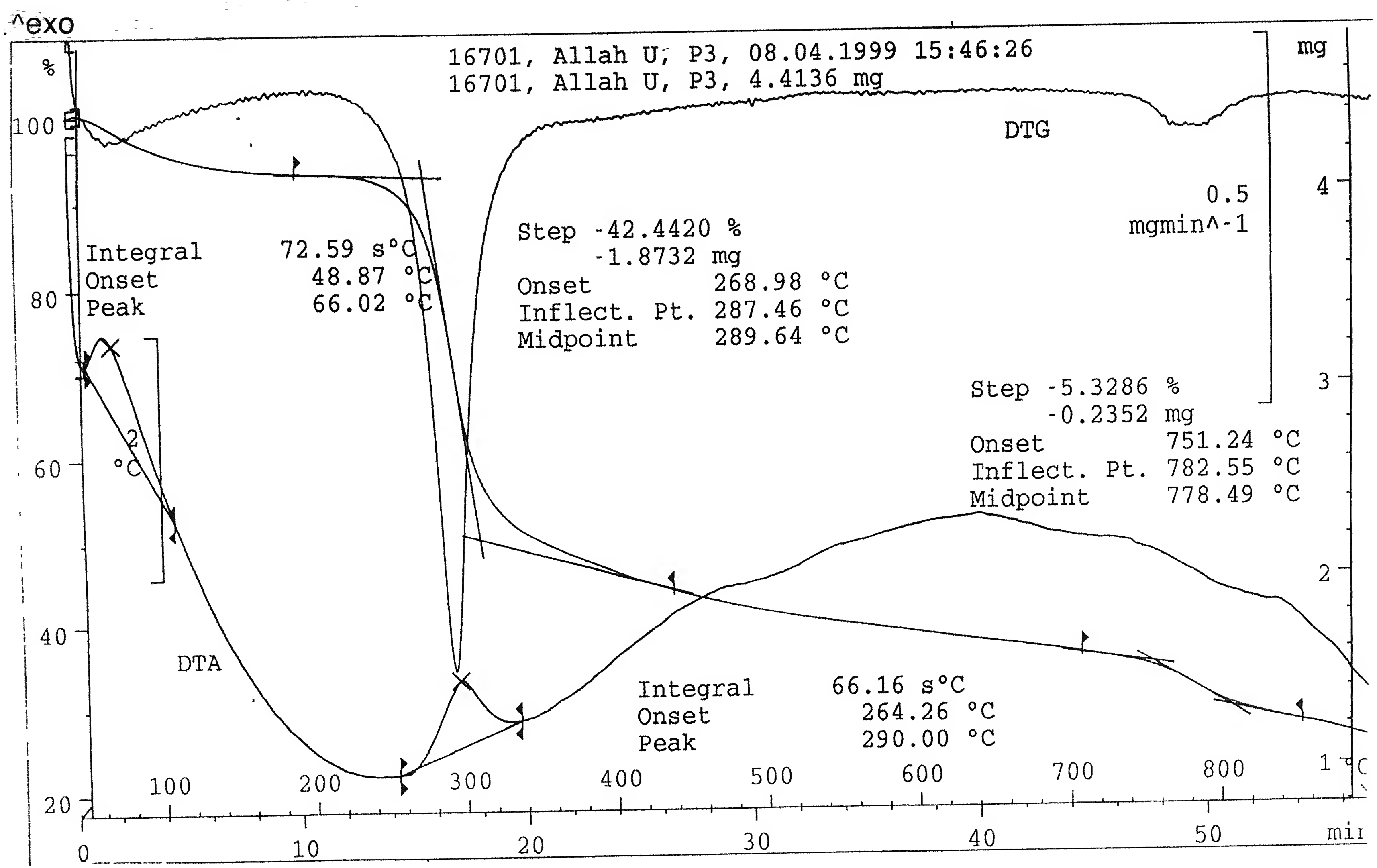


Fig 2.16 Thermogravimetric Trace of Xanthan Gum

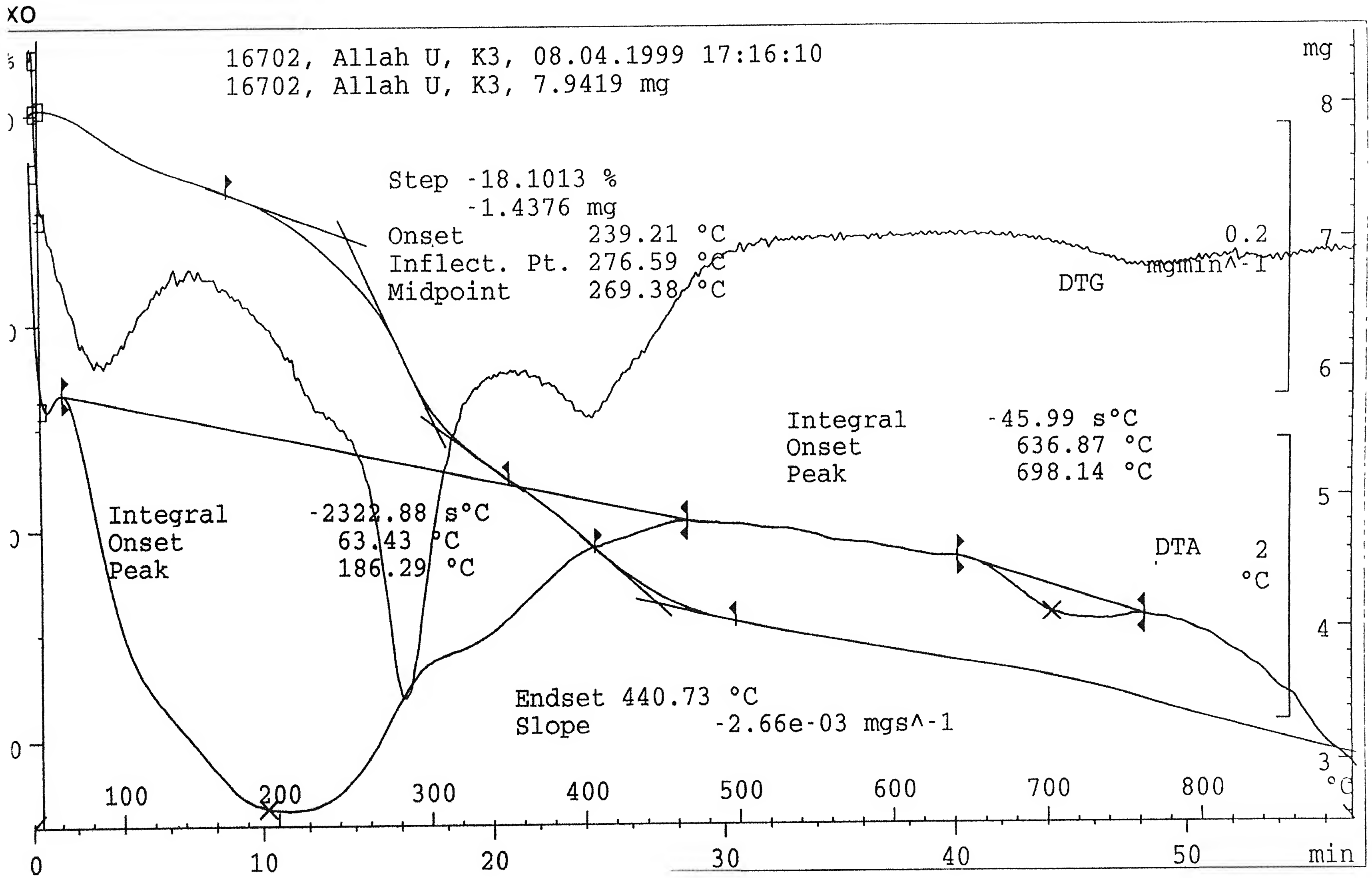


Fig.2.17 : Thermogravimetric Trace of Xanthan Gum-g-acrylamide

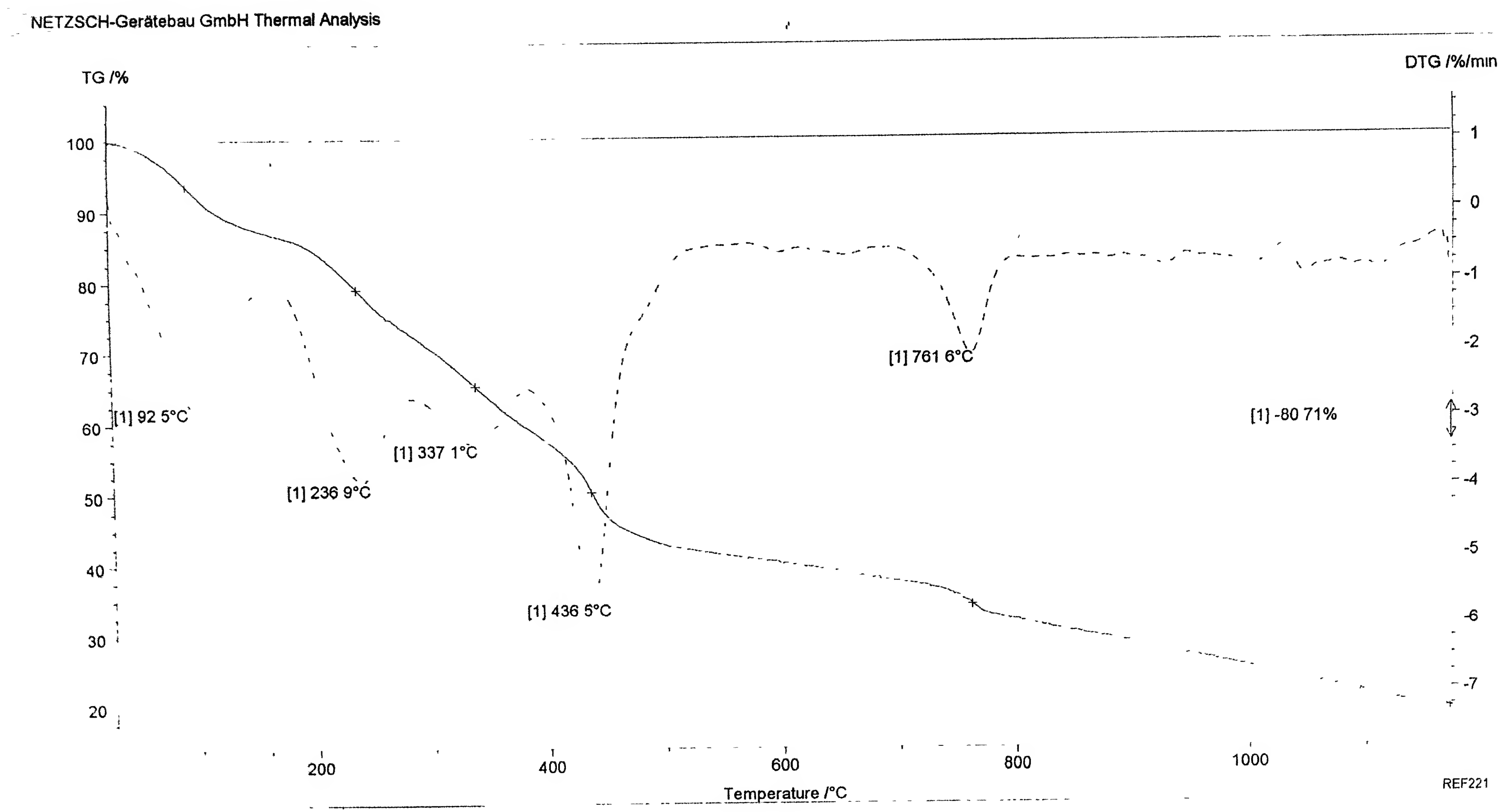
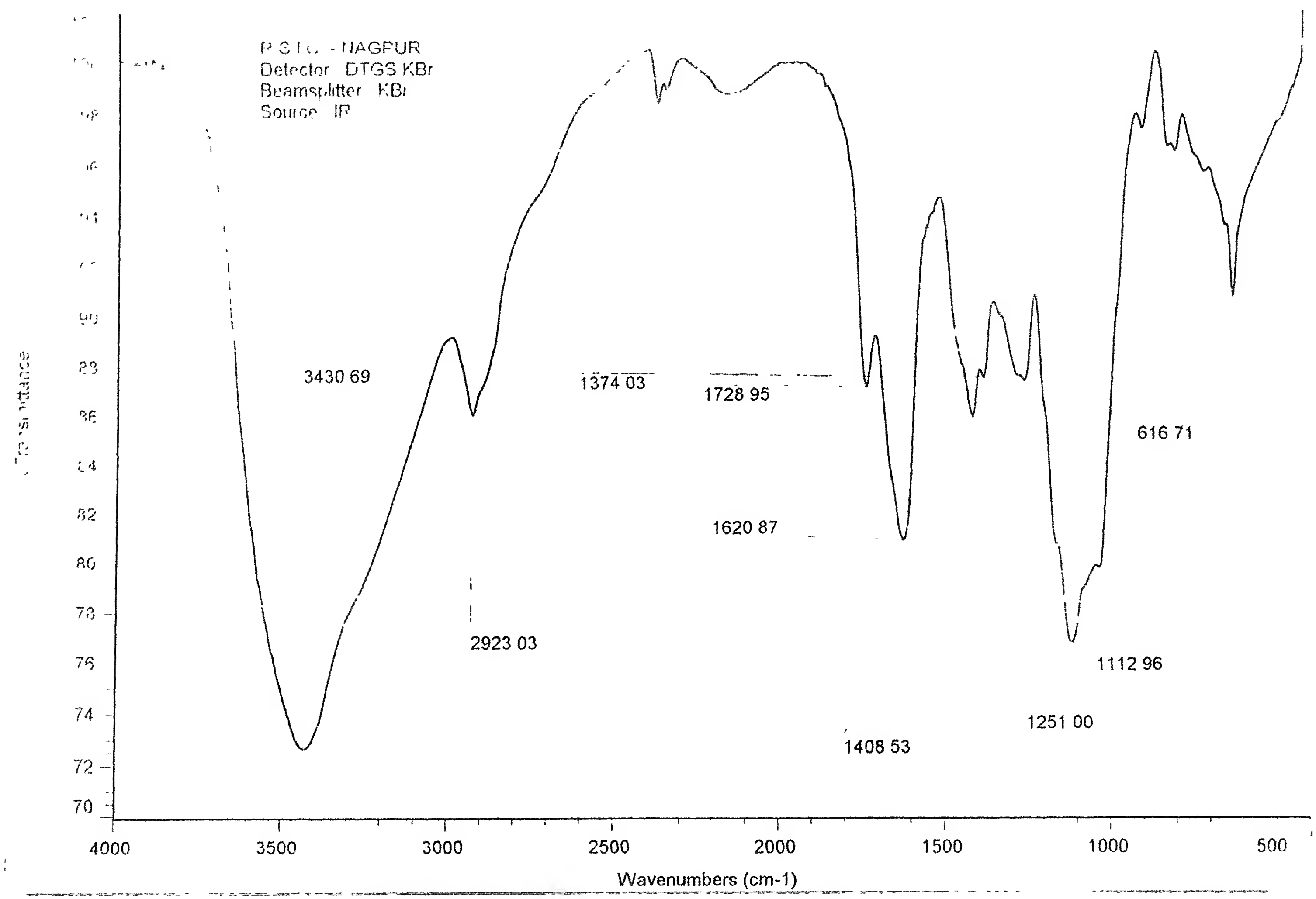


Fig.2.18 : Thermogravimetric Trace of Xanthan Gum-g-acrylic acid



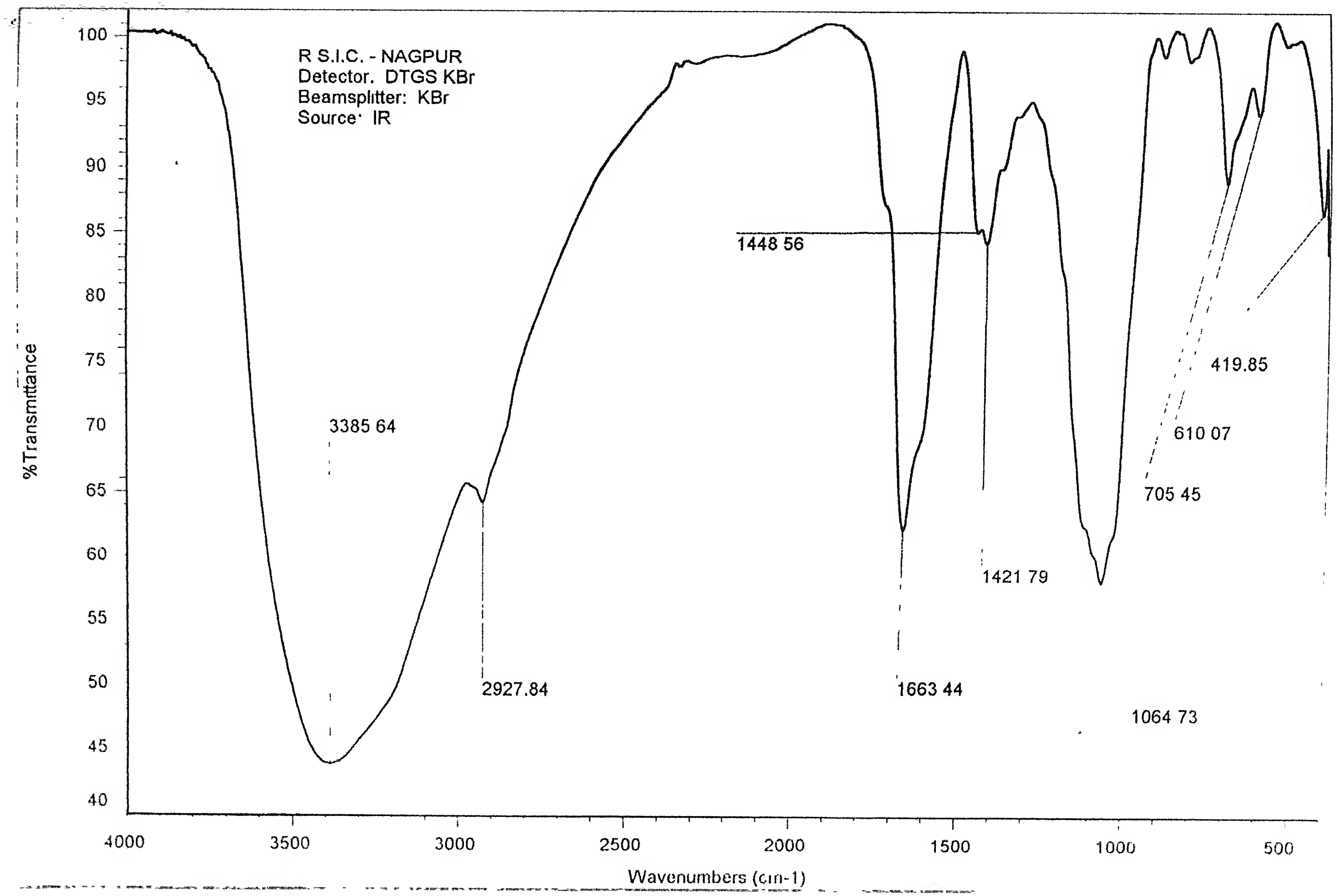
Date Tue Sep 29 13 36 28 1998

**W/O/No.-165, Sample code · [P1]

Scans 32

Xanthan Gum.

Resolution· 4 000



Date Tue Sep 29 13 14 09 1998

**W/O/No -165, Sample code . [K1]

Scans: 32

Yanthan Gum -g- Acrylamide

Resolution: 4.000

REFERENCES

1. Dintizes, F.R.; Babcock, G.E., and Tobin, R.; *Carbohydr. Res.* **13,** 257 (1970).

2 Holtzwarth, G.; *Carbohydr. Res.* **66,** 173 (1978).

3. Jansson, P.E.; Kenne, L. and Lindberg, B.; *Carbohydr. Res.* **45,** 275 (1975).

4. Melton, L.D.; Mindt, L.; Rees, D.A. and Sanderson, G.R.; *Carbohydr. Res.* **46,** 245 (1976).

5. Sutherland, I.; ed. *Surface Carbohydrates of the Prokaryotic Cell,*Academic Press, Inc , New York, **1977**, pp. 27-96.

6. Holtzwarth, G. and Ogletree, J.; *Carbohydr Res.* **76,** 277 (1980).

7. Jeanes, A; Pettsley, J.E. and Senti, I.R.; *J. Appl. Polym. Sci* **5,** 519 (1961).

8. Silman, R.W. and Rogovin, P; *Biotechnol. Bioeng.* **12,** 75 (1970); 14, 23 (1972).

9. Davidson, I.W., *FEMS Microbiol Lett.* **3,** 347 (1978).

10. Rees, D.A.; *Biochem. J.* **126,** 257 (1972).

11. Moorhouse, R.; Wilkinshaw, M.D. and Arnott, S., eds. *Extracellular Microbial Polysaccharides, ACS Symp Ser. No,* ***45,*** American Chemical Society, Washington, D.C., 1977, p.p. 284-298.

12. Jeanes, A. in Bikales, N.M. ed., *Water Soluble Polymers,* Plenum Press, New York, **1973**, p.p. 227-242.

13. Jeanes, A in Frisch, K.C.; Klempner, D. and Patsis, A.V. eds., *Polyelectrolytes, Technomic Puble.* Co., Inc., Westport, Conn., **1976,** pp

207-225.

14. Kang, K.S. and Cottrell, I. in H.J. Peppler and Perlman,D.; eds. *Microbial Technology 2nd ed.* Vol.**1**, Academic Press, Inc., New York, **1979**, p.p. 417-481.

15. Holtzwarth, G.; *Biochemistry* **15**, 4333 (1976).

16. Rogovin, S.P.; Anderson, R.G.; Coadmus, M.C.; *J Biochem. Microbiol Technol. Eng.* **3**, 51, (1961).

17. Kang, K.S. and Cottrell, I. in Peppler, H.J. and Perlman, eds., *Microbial Technology, 2nd* ed., Vol.**1**, Academic Press, Inc., New York, **1979**, pp. 417-481.

18. Jeanes, A in Frich, K.C.; Klempner, D. and Patsis, A.V. eds., *Polyelectrolytes, Technomic Publ Co, Inc, Westport, Conn*, **1976**, p.p. 207-225.

19. Slodki, M.E.; and Cadmus, M.C.; *Adv. Appl. Microbiol.* **23**, 19 (1978).

20. Snow, P. and Demain, A.L.; *Appl Environ. Microbiol.* **37**, 1186 (1979).

21 Cadmus, M.C.; Knuston, C.A.; Lagoda, A.A.; Pittsley, J.E. and Burton, K.A.; *Biotechnol Bioeng.* **20**, 1003 (1978).

22. Davidson, I.W ; *FEMS Microbiol. Lett.* **3**, 347 (1978).

23. Wells, J.; *FEMS Microbiol. Lett.* **3**, 299-314 (1978).

24. Kang, K.S.; Cottrel, I. in Peppler, H.J. and Perlman, D., eds., *Microbial Technology, 2nd ed*, Vol.1, Academic Press, Inc., New York, **1979**, pp. 417-481.

25. Szczesniak and Farkas, E.; *J. Food Sci,* **27**, 381 (1962).

26 Dea, I.C.M. and Mossis, E.R., in Sandford P, and Laskin, A. eds,

Extracellular Microbiol., Polysaccharides, ACS Symp. Ser No 45, American Chemical Society, Washington D.C 1977 pp 74-182

27 Andrew, T.R. in Sandford, P. and Laskin, A. eds, *Extracellular Microbial Polysaccharides, ACS Symp Ser No.45, American Chemical Society,* Washington, D.C. **1977**, pp. 231-241.

28. Kang, K.S. and Cottrell, I. in Peppler, H.J and Perlman, D. eds., *Microbial Technology, 2^{nd} ed*, Vol.**1**, Academic Press, Inc., New York, **1979,** pp. 417-481.

29 Sandvik, E.I. and Maerker, J.M.; Jeanes, A. in Sandford, P. and Laskin, A. eds, *Extracellular Microbial Polysaccharides, ACS symp. Ser. No.45*, American Chemical Society, Washington, D.C.,**1977**, pp. 242-264.

30 Wells, J.; Jeanes, A. in Sandford, P. and Laskin, A. eds, *Extracellular Microbial Polysaccharides, ACS symp Ser No.45*, American Chemical Society, Washington, D.C.,**1977**, pp. 299-314.

31. Ellitt, J.H, ;Jeanes, A. in Sandford, P. and Laskin, A. eds, *Extracellular Microbial Polysaccharides, ACS symp. Ser. No.45*, American Chemical Society, Washington, D.C.,**1977,** pp. 144-159.

32. Sandvik, E.I. ;,Maerker, J.M.; Jeanes, A. in Sandford, P. and Laskin, A. eds, *Extracellular Microbial Polysaccharides, ACS symp Ser. No.45*, American Chemical Society, Washington, D.C.,**1977**, pp. 242-264.

33. Sasajawa, Hirosaku (Marufuku Yushi Kogyo K.K.) *Jpn. Kokai Tokkyo Koho J.P.* 03,247,699,[91,247,699](Cl.C11B15/00)05 Nov. **1991,** Appl. 90/45006, 26 Feb. 1990, 2pp.

34. Pillico, Michael, A U.S. US 5,073, 363 (Cl. 424-49, A61K7/16, 17 Dec. 1991, US Appl. 418, 251, 06 Oct. 1989; 5 pp. Cont.-in-part of U.S. 5,071, 637.

35. Dumitriu, Severjan; Dumitriu, Marea (Polytech. Inst. Iasi, R-6600 Iasi, Rom.). *Biomaterials* 1991, **12(9)**, 821-6 (Eng.).

36 Ueda, Shuichiro (Yakult Honsha Co. Ltd.) *Jpn.Kokai Tokkyo Koho* JP03,292,854[91,292,854](Cl.A23C0/152), 24 Dec. 1991, Appl. 90/93, 975, 11 Apr. 1990; 3pp.

37 Cuvelier, G.; Peigney-Noury, C.; Launay, B. (ENSIA, 91305 Massy, Fr.). Gums Stab Food Ind.5, [Proc. Int. Conf], 5th 1989 (Pub. 1990), 549-52 (Eng.) Edited by Phillips, Glyn Owain; Williams, Peter Anthony; Wedlock, David J. IRh.; Oxford, U.K

38 Farrar, David: Flesher, Peter; Symes, Kenneth Charles (Allied Colloids Ltd.) Eur. Pat. Appl Ep 284, 367 (Cl. CO8 F 251/00), 28 Sep. 1988, G.B. Appl. 87/7, 251, 26 Mar. 1987; 5 pp.

39. Wu, G.S.; Yanxia, L.O.; Zhaing, G ; *Chin Julin Dexue Ziren Kexue Xueba* **(3)**, 123 (1988).

40. Cai, Z.; Wag, Z.; Pan, S.; *Zhongguo Zaazhi,* **9(4)**, 37 (1990).

41. Wu, G.S.; Yanxia, Lo; Zhaing, G; *Chin Julin Dexue Ziren Kexue Xueba* **(3)**, 123 (1988).

42. Ranby, B. and Zuchowska, D.; *Polym. J.* **19(5)**, 623 (1987).

43. Singh, O.P.; Sandle, N.K. and Varma, I.K.; *Die Angewandte Makromolekulare Chemie* **121**, 187 (1984).

44. Singh, R.P.; Jain, S.K.; in *Polymer Science, Contemporary Themes, Vol. II* (Sivrams Ed.) Tata McGraw Hill Publishing Co. Ltd., New Delhi, **(1991)**, pp.776.

45. Prasad, P.N ; Mark, J.E.; Fai, T.J.; *in Polymer and Advanced Materials: Emerging Technologies and Business Opportunities*, Plenum Press, New York; **(1995)**, pp. 227.

46. Kanan, K; Guar Gum Based *Graft Copolymers Flocculation and Rheological Behaviours* M.Tech. Thesis, I.I.T. Kharagpur **(1998)**.

47. Deshmukh, S.R.; Sudhakar, K.; Singh, R.P.; *J. Appl. Poly. Sci.***143**, 1091 (1991).

48. Behari, K.; Tripathi, M.; Taunk, K.; Kumar, R.; *Polym Int.* **49**, 153-157(2000)

49. Bıcak, Niyazi, Sherrington, David C.; Senkal, B. Filiz; *React Funct. Polym.*, **41(1-3)**, 69-76 (1999).

50. Bajpai, U.D.N. and Rai, S.; *Polym Sci* **35**, 1169 **(1988)**.

51. Fanta, G.F.; *'Block and Graft Copolymerization'* R.J. Ceresa ed. Wiley Inter Science, New York; 1, **1973**.

52. Morin, B P. and Rogovin, Z.A.; *J. Polym. Sci. (USSR);* **A 18 (10)**, 2451 (1976).

53. Mishra, B.N.; Dogra, R.; Kaur, I. and Jassal, J.K.; *J. Polym. Sci.; Polym. Chem Ed.* **17**, 1861 (1979).

54. Samal, R.K.; Nayak, P.L.; Nayak, M.C., *Die Angew Makromol. Chemic,* **80**, 95 (1979).

55. Samal, R.K.; Satrusallya, S.C.; Nayak, P.L. and Nand, C.N.; *J. Appl. Poly. Sci.* **28**, 1311 (1983).

56. Thomas, W.M.; Gleason, E.H. and Mino, G.; *J. Polymer Sci* **24**, 43 (1957).

57. Greenwald, H.L.; Luskin, L.K.S.; in Davidson, R.L. ed.; *'Handbook of Water soluble Gums and Resins'*, Mcgraw Hill, New York, Chapt. 17, pp. 1-19 **(1980)**.

58. Subramanian, Srinivas, Lee Sunggyu; *J Polym. Sci*, **70(5)**, 1001-1007 (1998).

59. Guo, Yuhai ; Zhang, Jianchur; Shi, M.; *J China, Text. Univ.*, **16(4)**, 84-87 (1999).

60. Yoshikawa, Masakazu; Motoi, Toshihiro; Tsubouchi, Keisuke; *J. Macromol Sci , Pure Appl Chem.* **A 36(4)**, 621-631 (1999).

61. Rao, G.S. Srinivas; Choudhary, M.S., Rao, K.V.; Anand, J.S.; Naqvi, M.K.; *Polym Sci.*, **1**, 106-11 (1994).

62. Bayazeed, A.; Elzairy, M.R and Hebeish, A.; *Starke* **41(6)**, 233 (1989).

63. Date, M ; Sumiya, T.; Tanka, K.; Zer offen DE 4,127,814 (Cl.C08F8/04), **(1992).**

64. Date. M.; Sumiya, T ; Tanka, K.; Ger Offen DE 4, 127, 889 (Cl.C08F6/04), **(1992)**

65. Hebeish. A ; Elzairy, M.R., Rafei, H M., Higazy, A. and Elsisy, E.; *Starke* **42(3)**, 98 (1991).

66. Cao, A.B., Song, R.; Wang, C.; *Huaxue Shijie*, **33(11)**, 19 (1992).

67. Mostafa. Kh. M.; *J Appl Polym Sci.* **56(2)**, 263-9 (1995).

68. Miyata, N.; Sakata, I.; *Jpn Kokkai Tokkyo Koho JP* 6397,612[8897, 612] (Cl. C08 251/00). (1988).

69. Morin. B.P. and Rogovin. Z.A.; *J. Polym. Sci. (USSR)*; **A 18(10)**, 2451 (1976).

70. Mishra, B.N ; Dogra, R., Kaur, I. and Jassal, J.K.; *J. Polym., Sci., Polym.Chem Ed.* **17**, 1861, (1979)

CHAPTER-III

Graft Co-polymerization of Acrylic Acid onto Dextran

1 Structure, Chemical Composition, Properties and Uses of Dextran.

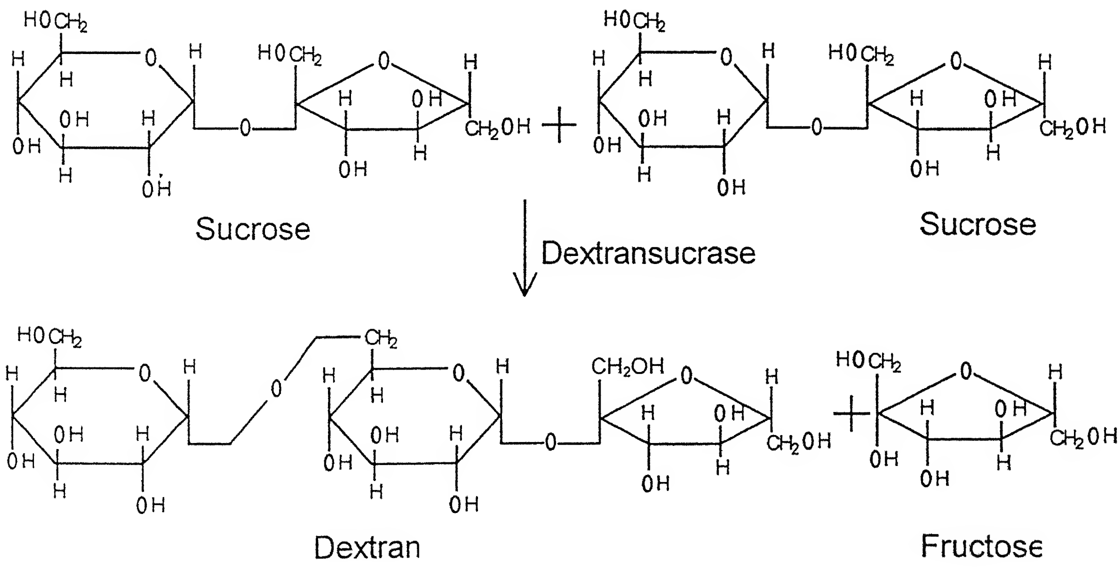
2. Graft Co-polymerization of Acrylic Acid onto Dextran by Potassium peroxydiphosphate (PDP) / Ag(I) Redox Pair.

1. STRUCTURE, CHEMICAL COMPOSITION, PROPERTIES AND USES OF DEXTRAN:

Dextran is α-D-glucan in which 1→6 linkages predominate, *i.e.* 50% or more of the α-D-glucopyranosyl residues are linked as such. Dextran is synthesized by a large number of microorganisms or enzymes elaborated by it and exhibits a wide spectrum of properties depending on its microbial origin.

The early history of dextran reaches back to studies in the mid-nineteenth century; the name destran was coined by Scheibler in 1869. Tarr and Hibbert[1] published the first detailed study of optimal conditions for the preparation of dextran.

Biosynthesis of dextran from sucrose was the first direct enzymic polymerization demonstrated for a disaccharide donor substrate[2]. The reaction is catalyzed by an inducible enzyme dextransucrase:



Sucrose is the only donor substrate known and it is the initial acceptor; repetitive α-D-glucopyranosyl transfer occurs so rapidly that high molecular weight products are formed without detectable oligosaccharide intermediates.

See References On Page No. 84-88

On the basis of methylation fragmentation analysis, an average repeat unit structure for dextran can be written as in fig. (3.1).

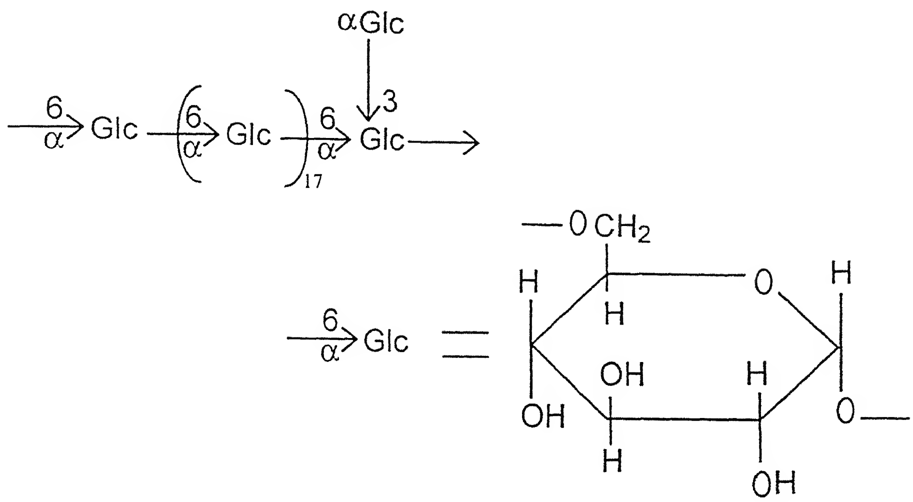


Fig. 3.1 : Structure of Dextran.

where Glc represents a D-glucopyranosyl residue. However, according to chemical degradation studies, only about 85% of the side chains are 1 or 2 glucosyl residues in length[3]. Enzymic degradations indicate that the remaining 15% of the side chains may have an average length of 33 glucosyl residues and may not be distributed uniformly in the molecule[4]. This highly irregular structure, if considered with the flexible coil conformation assumed by α-(1$\rightarrow$6) linked glucans in solution, could account for low viscosities even though light-scattering measurements suggest weight average molecular weight $\overline{Mw}$ values of (35-50) x 10^{-6} [5-6]. Determination of number average molecular weight $\overline{Mn}$ value for dextran gives much lower value and suggests that the high value of $\overline{Mw}$ reflects molecular aggregation[7]. The non (1$\rightarrow$6) linkages are of two types, the (1$\rightarrow$4)-like and the (1$\rightarrow$3)-like.

PRODUCTION:

Although dextran has frequently been encountered as slimes incidental to the wine and sugar industries. There are considered as nuisances rather than a source of a useful product. Therefore the dextran of commerce are the result of specific fermentation processes developed for their manufacture.

There are two main methods available for fermentation, the whole culture process and the cell free enzymatic process. The organism most widely used in U.S for both of these processes are strains of 'Leuconostoc mesenteroides' or 'Leuconostoc dextranicum. The Northern Utilization Research and Development Division (NURDD) of the U.S. Department of Agriculture has been active in classifying the various strains of dextran producing organisms[8] The culture receiving most commercial study has been designated as NRRLB-512 strain of Leuconostoc mesenteroides. (In 1950) the β-512F substrain supplanted β-512 for all work at NURDD, but the old designation was retained. The dextrans from β-512 and β-512F appear to be identical).

PROPERTIES:

The specific rotation of dextran differs with the solvent. Thus NRRL β-512 dextran showed $(\alpha)_D^{25}$ + 199° (C. 1.0, water), + 203° (C. 1.0, N potassium hydroxide) and + 215 (C. 1.0, formamide)[8]. In general, a higher rotation accompanies an increase in (1→3)-like linkages.

The intrinsic viscosity in water at 25°C, of the dextran studied by Jeanes and Co-workers[8] varied over a range of 0.15-2.0. Even the highest of these viscosities are relatively low for polymers of such high molecular weight. No generalizations have been made which relate the influence of the type and proportion of the non-(1→6) links to the viscosity of dextran in

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water. However, there is a grouping of dextran possible by comparison of the viscosity parameter and (1→6) linkage content. Wales and co-workers[9,10] have attempted to correlate intrinsic viscosity with molecular shape in hydrolyzed dextran. Senti and Co-workers[11] also determined the viscosity, sedimentation and light-scattering properties of 24 fractions of acid-hydrolyzed NRRL B-512 dextran. The fractions varied in molecular weight from 17,700 to 19,500,00.

Wall and Childers[12] found the deffusion coefficient at 25°C for 1.5% dextran in 0 7M sodium chloride to be 5.1-5.4 x 10^{-7} cm^2 per sec. Ogston and Woods[13] showed that the dextran particles in solution are highly solvated and not very asymmetric and that this view is consistent with their chemical structure

USES:

1. *Pharmaceuticals:* While dextran and its derivatives were originally suggested mainly for industrial uses, by far the greater number of literature references are concerned with its medical use as a blood plasma extender. Clinical use of dextran as fractions having specific molecular size ranges is based on its comparability with human tissues and complete metabolic utilization, whether it is ingested or administered parenterally[14].

Dextran has been recommended for use[15] in connection with X-ray examination requiring an injected or ingested contrast agent. A mixture containing dextran of low molecular weight retains the contrast agent in the desired area for adequate X-ray study and then aids in complete elimination of the foreign material.

Water soluble dextran or its ethers are suggested[16] as additives in cosmetic body powders to increase their adhensiveness toward moist skin.

Dextran also functions as an added clearing agent when formulated in dental creams or other dentifrice preparations[17, 18] in amounts upto 3%.

2. ***Food:*** Biological tests have demonstrated that when dextran containing a high proportion of α-(1$\rightarrow$6) linkages is included in normal diet on a regular regimen, gain in body weight is inhibited. While dextran is edible and assimilated without unfavourable effect on the human systems, it appears that the α-(1$\rightarrow$6) linkages are enzymes present in the gastro-intestinal tract. An edible container, such as an ice cream cone, can be prepared[19] consisting essentially of dextran. The dextran film lengthens storage life and retards decay during thawing by absorbing the moisture.

3. ***Agricultural Uses:*** Individual seeds can be coated with a dextran film[20] in which a coloured dye and also a fungicide or insecticide can be incorporated if desired Dextran has been shown[21, 22] to have a beneficial effect in aggregating clay soil particles. Certain dextran products[23], when applied to the soil, have also enhanced seedling emergence, rate of plant growth and crop yields Soil conditioning can be brought about by synthesis of dextran in the soil when appropriate organisms are added[24].

4. ***Coating Uses:*** Dextran applied as a coating has diverse uses. When mixed with inorganic pigments as a carrier and extender [25], dextran makes a composition useful in water based enamels. A low molecular weight dextran is recommended as a finishing agents or size for textiles to improved appearance after ironing.

DEXTRAN DERIVATIVES AND THEIR USES:

Dextran has been modified for imparting it with special properties and uses some of these are.

1. ***Acetates:*** The conversion of dextran to a tribenzoate and triacetate was reported by Hibbert and co-workers[26]. Dextran acetate can be prepared by using acetic anhydride, glacial acetic acid and a sulphuric or phosphoric acid catalyst[27].

The triacetates of those dextrans having 50-80% of (1→6) linkages decompose at much lower temperatures than do those from dextrans with a higher proportion of (1→6) linkages. It was shown take that a film formed from NRRL B-512 dextran triacetate has low mechanical strength but is superior to films from a branched material, such as amylopectin triacetate.

2. ***Sulfates and Nitrates:*** Conversion of hydrolyzed dextran to sulphate esters by reaction with chloro-sulfonic acid in pyridine was supported by Grönwall and Co-workers[28-30], by Ricketts[31] and by Payne and Baker[32]. These compounds, if sufficiently sulphated, show blood anticoagulant activity.

3. ***Alkyl and Benzyl Ethers:*** The etherification process involve treatment of the fermented culture medium or isolated dextran[33, 34] in an alkaline solution with alkyl or arylalkyl halides and chlorohydrins, usually at 80-85°C for several hours. Dextran butyl ether thus obtained can be esterified with benzoyl chloride[35] to give mixed ether esters.

Benzyl dextran or a blend of at least 50% of dextran benzyl ether and an ester of dextran with a higher saturated fatty acid[36] is a useful lacquer ingredient when dissolved in a volatile solvent.

Cotton yarn can be impregnated with dextran ethers[37]. This yarn can be further alkylated in an alkaline solution and finally heated at 130-140°C to complete the alkylation. The resultant yarn is shrink-resistant and moisture proof[38]

MISCELLANEOUS:

Glycosides obtained by alcoholysis of native dextran[39] have been suggested as acceptable blood plasma extenders. The carboxy (C_{1-4}) alkyl dextran polyalc.,has been used as drug complex[40]. The reaction between the carboxylated dextran derivative and the medicinal compound bonded to spacer etc., can be effected to achieve a high yield and side reactions can be inhibited in the case where, for example, the medicinal compound is one having a lactose ring.

2. GRAFT COPOLYMERIATION OF ACRYLIC ACID ONTO DEXTRAN BY PDP/Ag(I) REDOX PAIR:

Modification of natural polymers through graft copolymerization has been an interesting technique for improving their properties to make them industrially useful By the process of graft copolymerization the physical and chemical properties of a synthetic macromolecule are superimposed on the properties of natural polymer

Acrylic acid possesses some unique characteristics and reactivities and the polymers derived from it find many industrial applications. One of the earliest applications of poly (acrylic acid) was in thickening. Thickening action in water may be used in secondary recovery of petroleum in oil fields, toothpaste, hydraulic fluids and even liquid rocket-fuels have been gelled using acrylic acid polymers[41] Cross linked acrylic acid polymers as ion exchange resins have been used in recovery of antibiotic and sugar manufacture. Polymers of acrylic acid can be formulated to impart green strength to molded articles such as ceramics or foundry core business. It also serves several functions in adhesives manufacture.

Graft copolymerization of acrylic acid has been studied on various, synthetic and natural polymeric substrate. Graft copolymer of acrylic acid onto maize starch using $K_2S_2O_8$ as free radical initiator were prepared under different conditions[42]. Acrylic acid graft copolymer showed marked improvement in the water retention capacity[43-44]. Polyacrylic acid starch composite has been reported to behave as a substitute for sodium alginate in printing cotton fabrics with reactive dyes[45]. Graft copolymerization of acrylic acid onto starch has been carried out different conditions with $(NH_4)_2S_2O_8$ as catalyst[46]. It has been observed that fabric samples, sized with graft copolymer obtained by graft copolymerization of acrylic acid onto rice starch using potassium permanganate/oxalic acid redox system as

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initiator, have more break and abrasion resistance than that sized with native rice starch[47]. Legnen-grafted acrylic acid copolymers are very good absorbents and are used as water retention agents for soils[48]. Thus it is evident that polyacrylic acid has wide range of applications in various fields. Dextran also enjoys a wide range of applications in industries such as mining, paper and textile industry and in oil wells etc. Thus it was thought worthwhile to graft acrylic acid onto dextran so as to produce a graft copolymer which has improved indusrial applications.

Potassium peroxydiphosphate is an inorganic compound containing peroxide bond, it is isoelectronic and isostructural with peroxydisulphate ion and the oxidation/reduction potential of $P_2O_8^{-4}$ is found to be -2.01 V. Although extensive oxidation[49] and polymerization[50-52] have been carried out using peroxydisulphate ($S_2O_8^{2-}$) but little is known about the chemistry of peroxydiphosphate ($P_2O_8^{4-}$). A survey of the literature reveals that the oxidation by peroxydiphosphate ion has been reported by Edward et al.[53]. Hariharan and Meenakshi[54] have reported the polymerization of acrylonitrile initiated by PDP-Ag^+ system and during later studies[55-57] it was found that PDP is a better initiator for vinyl polymerization than peroxydisulphate ion. Further this new initiator coupled with Fe(II), Mn(II), thiourea, tartaric acid and fructose[58-61] was used for grafting vinyl monomers onto a number of natural and synthetic fibres. Graft copolymerization with this redox pair results in low amount of homopolymer and high percentage of grafting.

EXPERIMENTAL:

Materials:

Acrylic acid (Aldrich) was freshy distilled over copper turning under vacuum and the middle fraction was used. Potassium peroxydiphosphate was

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received as a gift sample from FMC, USA. $AgNO_3$ (E. Merck) was used as such. Dextran (Sigma) was used as such. Triple distilled water was used as reaction medium.

Graft Copolymerization:

Dextran solution was prepared by addition of weighed amount of dextran to 50ml. of triple distilled water in a reactor. A definite amount of HNO_3 (dil), $AgNO_3$ and acrylic acid solutions were added to the reactor and kept at constant temperature The nitrogen gas was allowed to pass through the solution in the reactor and the PDP solution. After half an hour PDP solution was added to initiate the reaction After the specified time of reaction, the reaction was stopped by letting air in the reactor. The reaction mixture was poured in a water methanol mixture where grafted and ungrafted dextran precipitate out and polyacrylic acid remains in the solution. The precipitate was separated dried and weighed. The polyacrylic acid was precipitated out by acidifying the filtrate. The polyacrylic acid thus formed as by product is separated dried and weighed.

RESULT AND DISCUSSION:

The graft copolymer has been characterised according to Fanta's definition as discussed earlier. The effect of PDP, $AgNO_3$, hydrogen ion, dextran and acrylic acid concentration as well as time and temperature on grafting parameters have been studied.

Effect of Potassium Peroxydiphosphate Concentration:

Tabel (3.1) exihibits the effect of PDP concentration. The grafting ratio, add on and efficiency increase with the concentration whereas homopolymer decreases (Figs. 3.2 & 3.3). This may be due to the fact that,

with increase in PDP concentration, the concentration of active species increase thereby increasing the concentration of primary free radicals resulting in greater amount of graft copolymer.

Effect of Silver Ion Concentration:

The effect of Ag^+ ion on grafting parameters has been studied by varying the concentration of $AgNO_3$ (Table 3.2). The grafting ratio, add on increase on increasing the concentration of $AgNO_3$ from $3.0x10^{-3}$ to $7.0x10^{-3}$ mol dm^{-3}, but on further increasing the concentration, these grafting parameters decrease (Figs.3.4 & 3.5). The grafting efficiency increase throughout the variation. This observation may be attributed to the increase in concentration of complex (A) which reacts with dextran molecule to give different free radicals as shown in eq. (2).

Effect of Acrylic Acid Concentration:

The effect of monomer concentration on grafting reaction has been studied at various concentration of acrylic acid (Table 3.3). The grafting ratio, add on and conversion increase as the acrylic acid concentration is increased from $6.0x10^{-2}$ to $14.0x10^{-2}$ mol dm^{-3} (Figs. 3.6 & 3.7). This observation may be attributed to the fact that acrylic acid exhibits the phenomenon of gelation and due to gelation the movement of growing polymeric chains is restricted leading to lowering of termination and hence the increase in the grafting ratio, add on and conversion.

Effect of Hydrogen ion Concentration:

The grafting reaction has been conducted at various hydrogen ion concentrations and the results have been summarised in Table 3.4. Grafting ratio, efficiency, conversion, and add on increase with the increasing concentration of hydrogen ion upto 8 $0x10^{-2}$ mol dm^{-3}. Thereafter the value

of these parameters decrease with the hydrogen ion concentration (Figs. 3.8 & 3.9). This observation can be explained on the basis of the fact that upto 8.0×10^{-2} mol dm^{-3} of hydrogen ion concentration, active species such as $H_2P_2O_8^{2-}$ or $H_3P_2O_8^{-}$ are formed which interact with Ag^+ to form a complex, which reacts with dextran molecule to give different free radicals. These free radicals enhance the grafting. With the increase in the concentration beyond 8.0×10^{-2} moles dm^{-3}, less active species such as $H_5P_2O_8^{+}$ and $H_6P_2O_8^{2+}$ might be formed, thereby decreasing the grafting parameters.

Effect of Dextran Concentration:

The effect of dextran concentration on grafting parameters has been studied by varying the dextran concentration from 1.2 to 2.8 g dm^{-3} (Table 3.5). Grafting ratio, add on and efficiency increase on increasing the dextran concentration upto 2.0 g dm^{-3}, thereafter a decreasing trend is observed (Figs. 3.10 & 3.11). Conversion however increases continuously. It may be due to availability of more and more grafting sites with increase in dextran concentration, but after the cited concentration, the increase in viscosity may restrict the accessibility of the monomer to the growing polymeric chain at the active sites leading to the decrease in grafting.

Effect of Time Period:

The grafting reaction has been carried out for different time intervals (Table 3.6). Grafting ratio, add on and efficiency increase with increase in time upto 150 min and decrease thereafter (Figs. 3.12 & 3.13). This behaviour may be explained on the basis that within 150 min. all the active sites are exhausted and beyond this time period mutual annihilation of growing grafted chains occur leading to termination.

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Effect of Temperature:

The grafting reaction has been carried out at various temperatures ranging from 30°C to 45°C (Table 3 7) The grafting ratio, add on and conversion increase with temperature (Figs. 3.14 & 3.15). At higher temperature, it is very likely that PDP may decompose giving rise to free radicals such as $PO_4^{2-\bullet}$, $HPO_4^{-\bullet}$ These free radicals are capable of abstracting hydrogen atom from dextran backbone resulting in the increase in grafting ratio, add on and conversion.

EVIDENCE OF GRAFTING:

IR Spectra:

On comparing the IR spectra of dextran and dextran-g-acrylic acid following additional peaks in the spectra of dextran-g-acrylic acid has been observed.

Band due to C=O stretching vibrations has been observed at 1750 cm^{-1}. A peak due to OH bending vibrations appeared at 1384.2 cm^{-1}. The broad band centered at 2925.5 cm^{-1} is attributed to stretching vibrations of OH bond. The presence of these bands confirm the grafting of acrylic acid onto dextran backbone.

Thermal Degradation Behaviour of Dextran

The degradation of dextran started at about 200°C. The degradation occured in single stage i.e. from 222.8 to 311.0°C. Its PDT and FDT are 222.8°C and 344.0°C respectively Graft copolymerization of acrylic acid onto dextran decreases the initial decomposition temperature while increases its final decomposition temperature. IPDT was found to be 313.9°C, which is greater than that of graft copolymer Table 3.8 and 3.9 reveal that

decomposition temperature beyond 40% weight loss is quite high and weight loss beyond 400°C is very high in comparison to grafted sample. The T_{max} was found to be 311.0°C. A char yield of 20% was observed at 730°C (Fig.3.16).

Thermal Degradation Behaviour of Dextran-g-Acrylic Acid:

Dextran-g-acrylic acid graft copolymer has been obtained by grafting acyrlic acid onto dextran using PDP/Ag^+ redox pair.

The graft copolymer began to degrade at about 140°C. However 0.7% weight loss occured was 100°C, which may be attributed to the absorbed water. The degradetion appears to be two-stage process i.e. from 140.9 to 258.0°C, and from 258.0 to 352.9°C. The T_{max} was found to be 352.9°C. The PDT was found to be 140.9°C. The final decomposition temperature (FDT) was observed at 352.9°C. The IPDT has been found to be 282.4°C. Table 3.8 and 3.9 reveal that weight loss beyond 300°C is quite significant. The char yield of 30% was obtained at 870°C (Fig. 3.17).

MECHANISM:

In a system containing PDP. Ag^+, Dextran, monomer and hydrogen ion, $P_2O_8^{4-}$ interacts with H^+ giving rise to various protononated species. $H_2P_2O_8^{2-}$ the most active species forms a complex with Ag^+, which interacts with dextran molecule giving rise to dextran free radical, HPO_4^- and $H_2PO_4^-$ free radicals.

Formation of Free radicals:

$$H_2P_2O_8^{2-} + Ag^+ \rightarrow H_2AgP_2O_8^- \quad (1)$$

Complex (A)

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$$H_2AgP_2O_8^- + DOH \rightarrow DO^\bullet + HPO_4^{-\bullet} + H_2PO_4^- + Ag^+ \quad (2)$$

$$DOH + HPO_4^- \rightarrow DO^\bullet + H_2PO_4^- \quad (3)$$

Initiation:

$$DO^\bullet + M \rightarrow DO\,M_1^\bullet$$

$$R^\bullet + M \rightarrow RM_1^\bullet$$

(Where $R^\bullet = HPO_4^{-\bullet}$, M = Monomer)

Propagation:

$$DOM_1^\bullet + M \rightarrow DOM_2^\bullet$$

$$DOM_2^\bullet + M \rightarrow DOM_3^\bullet$$

....

....

....

$$DOM_{n-1}^\bullet + M \rightarrow DOM_n^\bullet$$

$$RM_1^\bullet + M \rightarrow RM_2^\bullet$$

....

....

....

$$RM_{n-1}^\bullet + M \rightarrow RM_n^\bullet$$

Termination:

$$DOM_n^\bullet + DOM_m^\bullet \rightarrow \text{graft copolymer}$$

$$DOM_n^\bullet + RM_n^\bullet \rightarrow \text{graft copolymer}$$

$$RM_n^\bullet + RM_m^\bullet \rightarrow \text{Homopolymer.}$$

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Table 3.1

Effect of PDP

$[Ag^+] = 5.0 \times 10^{-3}$ mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3};
$[H^+] = 8.0 \times 10^{-2}$ mol dm^{-3}; [Dextran] = 2.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S.N	[PDP]x10^2 mol	% G	% A	% C	% E	% H
1	1.0	278.6	73.5	94.0	82.3	17.7
2.	2.0	285.1	74.0	90.6	87.4	12.6
3	3.0	321.3	76.3	97.9	91.1	8.9
4.	4 0	330.6	76.7	96.1	95.6	4.4
5.	5.0	340.1	77.2	95.6	98.8	1.2

Table 3.2

Effect of Silver Ion

[PDP] = 2.0×10^{-2} mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3};
$[H^+] = 8.0 \times 10^{-2}$ mol dm^{-3}; [Dextran] = 2.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S.N.	[Ag$^+$] x10^3 mol dm^{-3}	% G	% A	% C	% E	% H
1.	3.0	258.4	72.1	91.1	78.8	21.2
2.	5.0	285.1	74.0	90.6	87.4	12.6
3.	7.0	290.6	74.4	89.4	90.3	9.7
4.	9.0	255.6	71.8	75.2	94.4	5.6
5.	11.0	234.4	70.1	65.7	99.1	0.9

Table 3.3

Effect of Acrylic Acid

[PDP] = 2.0 x 10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0 x 10^{-3} mol dm^{-3};
[H^{+}] = 8.0x10^{-2} mol dm^{-3}; [Dextran] = 2.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S N.	[AA]x10^{2} mol dm^{-3}	% G	% A	% C	% E	% H
1	6.0	135.6	57.5	84.1	74.6	25.4
2	8.0	230.3	69 7	88.5	82.5	17.5
3.	10.0	285 1	74.0	90.6	87.4	12.6
4	12 0	340 3	77.2	96.7	81.5	18.5

Table 3.4

Effect of Hydrogen Ion

[PDP] = 2.0 x 10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0 x 10^{-3} mol dm^{-3};
[AA] = 10.0x10^{-2} mol dm^{-3}; [Dextran] = 2.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S N.	[H^{+}] x 10^{2} mol dm^{-3}	% G	% A	% C	% E	% H
1	2 0	201.4	66.8	70.2	79.8	20.2
2.	6.0	241.6	70.7	80.4	83.5	16.5
3	8.0	285 1	74.0	90.6	87.4	12.6
4	10.0	236.7	70.3	68.7	95.6	4.4
5	12.0	205 6	67.3	66.7	85.5	14.5

Table 3.5

Effect of Dextran

[PDP] = 2.0 x 10^{-2} mol dm^{-3}; [Ag^+] = 5.0 x 10^{-3} mol dm^{-3};
[H^+] = 8.0x10^{-2} mol dm^{-3}; [AA] = 10.0 mol dm^{-3};
Time = 120 min; Temp = 35°C.

S N	[Dextran] g dm^{-3}	% G	% A	% C	% E	% H
1.	1.2	198 5	66.5	46 7	70.8	29.2
2.	1.6	256 3	71.9	70.6	80.6	19.4
3.	2.0	285 1	74.0	90.6	87.4	12.6
4	2 4	240.1	70 6	97 1	82.4	17.6
5	2 8	190 1	65.5	99.2	74.5	25.5

Table 3.6

Effect of Time Period

[PDP] = 2.0 x 10^{-2} mol dm^{-3}; [Ag^+] = 5.0 x 10^{-3} mol dm^{-3};
[H^+] = 8.0x10^{-2} mol dm^{-3}; [Dextran] = 2.0 g dm^{-3};
[AA] = 10.0x10^{-2} mol dm^{-3}; Temp = 35°C.

S.N.	Time Period (Min.)	% G	% A	% C	% E	% H
1	60	201.7	66 8	78.1	71.7	20.3
2.	90	249.4	71.4	85.0	81.5	18.5
3.	120	285.1	74.0	90.6	87.4	12.6
4	150	331 4	76.8	97.1	94.8	5.2
5	180	302 6	75.1	99.1	84.8	15.2

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Table 3.7

Effect of Temperature

[PDP] = 2.0 x 10^{-2} mol dm^{-3}; [Ag^+] = 5.0 x 10^{-3} mol dm^{-3};
[H^+] = 8.0x10^{-2} mol dm^{-3}; [Dextran] = 2.0 g dm^{-3};
Time = 120 min; [AA] = 10.0 x 10^{-2} mol dm^{-3}

S.N	Temp. °C	% G	% A	% C	% E	% H
1	30	256.8	71.4	73.6	96.8	3.2
2.	35	285.1	74.0	90.6	87.4	12.6
3	40	300 1	75.0	97.4	85.4	14.6
4	45	314.7	75.9	99.2	88.1	11.9

Table 3.8

THERMOGRAVIMETRIC ANALYSIS OF GRAFT COPOLYMER

Sample Code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
G_1	222.8	344.0	311.0	313.9
G_2	140.9	352.9	352.9	282.4

Table 3.9

DECOMPOSITION TEMPERATURE (T°D)

Sample	T°D (°C) at following weight loss						
	10%	20%	30%	40%	50%	60%	70%
G_1	274.0	300.0	311.0	326.0	344.0	441.0	589.0
G_2	200.0	256.0	322.0	374.0	452.0	637.0	867.0

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Table 3.10

DECOMPOSITION TEMPERATURE (T^oD)

Temp (^oC)	Weight loss (%)	
	G_1	G_2
100	0.8	0.7
200	3.0	10.0
300	17.7	25.3
400	53.8	42.6
500	60.0	52.0
600	66.9	57.3
700	73.0	61.3
800	77.8	66.6

G_1 = Dextran

G_2 = Dextran-g-acrylic acid (PDP/Ag^+)

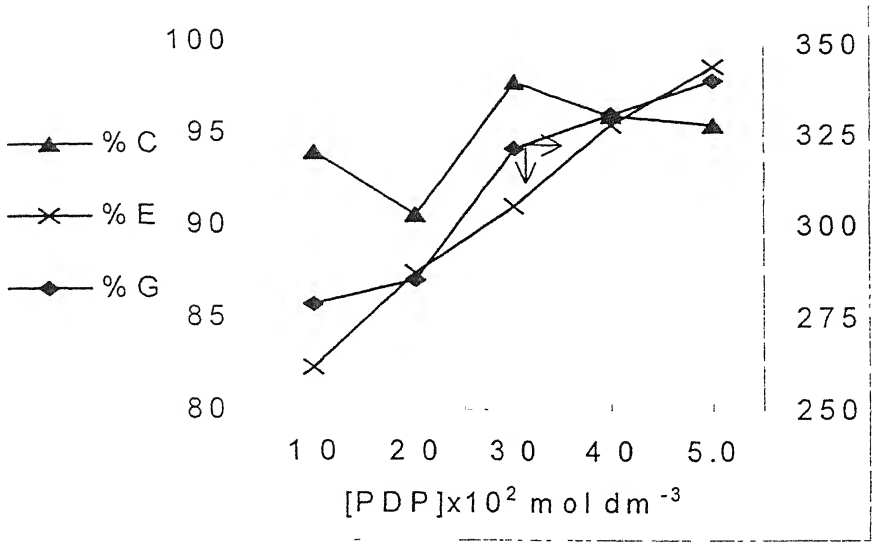


Figure 3.2 $[Ag^+] = 5.0\times10^{-3}$ mol dm^{-3}, [AA] = 10.0 $\times10^{-2}$mol dm^{-3}; $[H^+] = 8.0\times10^{-2}$ mol dm^{-3}; [Dextran] = 2.0 g. dm^{-3}; Time = 120 min. ; Temp = 35°C.

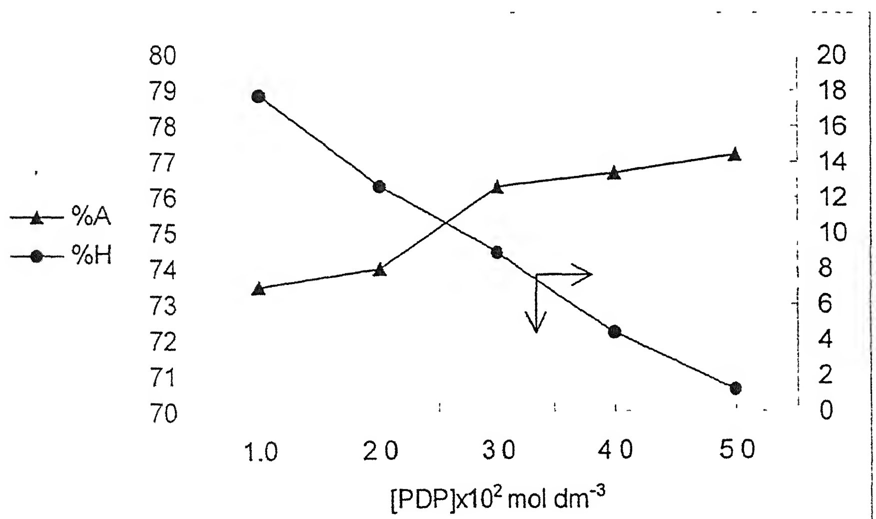


Figure 3 3 $[Ag^+] = 5.0\times10^{-3}$ mol dm^{-3}; [AA] = 10.0 $\times10^{-2}$mol dm^{-3}; $[H^+] = 8.0\times10^{-2}$ mol dm^{-3}; [Dextran] = 2 0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C

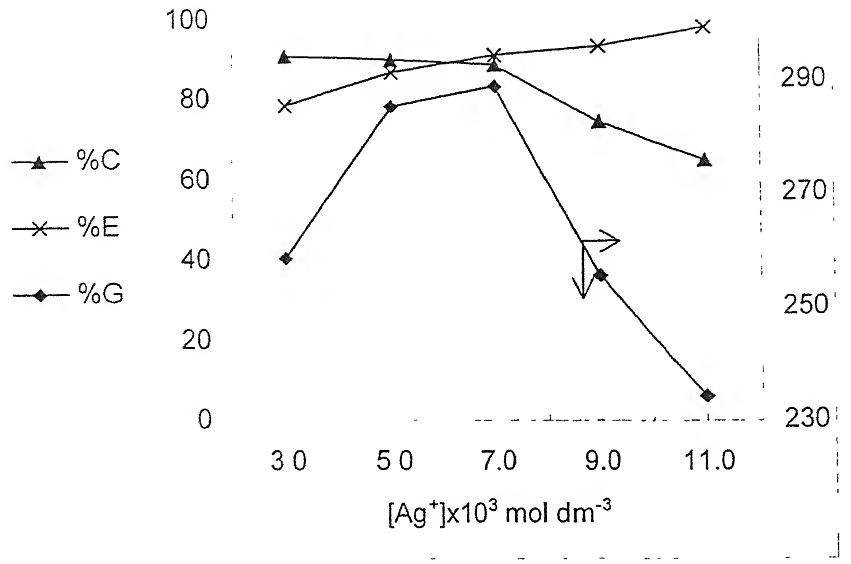


Figure 3 4 [PDP] = 2.0×10^{-2} mol dm^{-3}; [AA] = 10.0 $\times10^{-2}$mol dm^{-3}; [H^+] = 8.0×10^{-2} mol dm^{-3}; [Dextran] = 2.0 g dm^{-3}; Time = 120 min. ; Temp.= 35°C.

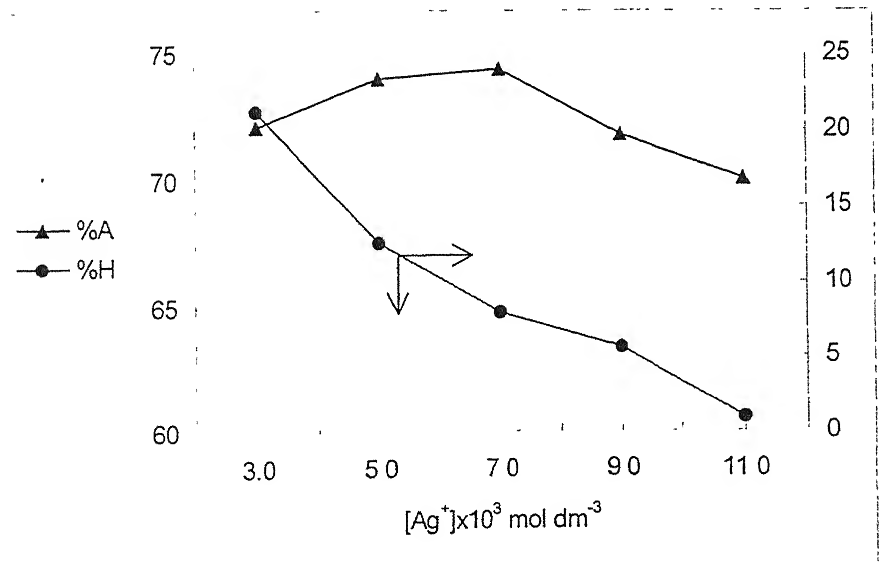


Figure 3.5 [PDP] = $2\ 0\times10^{-2}$ mol dm^{-3}; [AA] = 10.0 $\times10^{-2}$mol dm^{-3}; [H^+] = 8.0×10^{-2} mol dm^{-3}; [Dextran] = 2.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

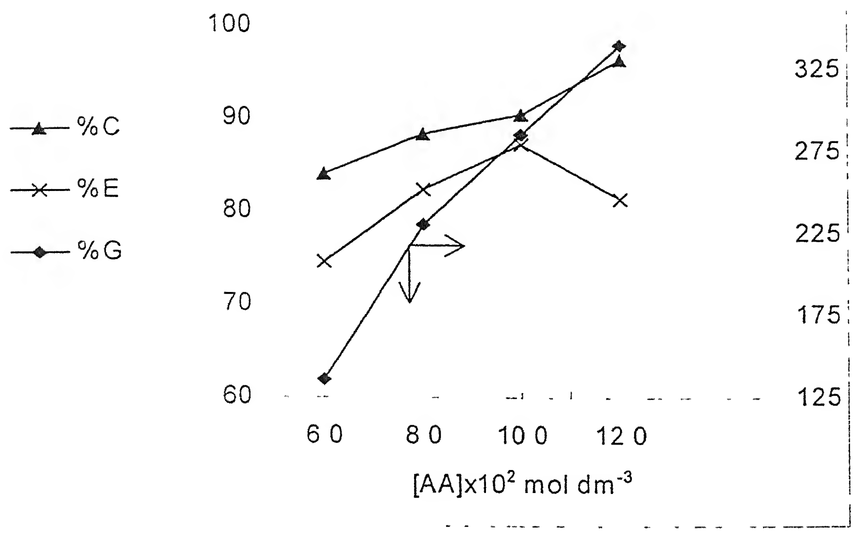


Figure 3 6 [PDP] = 2.0×10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0×10^{-3}mol dm^{-3}; [H^{+}] = 8.0×10^{-2} mol dm^{-3}; [Dextran] = 2.0 g. dm^{-3}; Time = 120 min ; Temp.= 35°C.

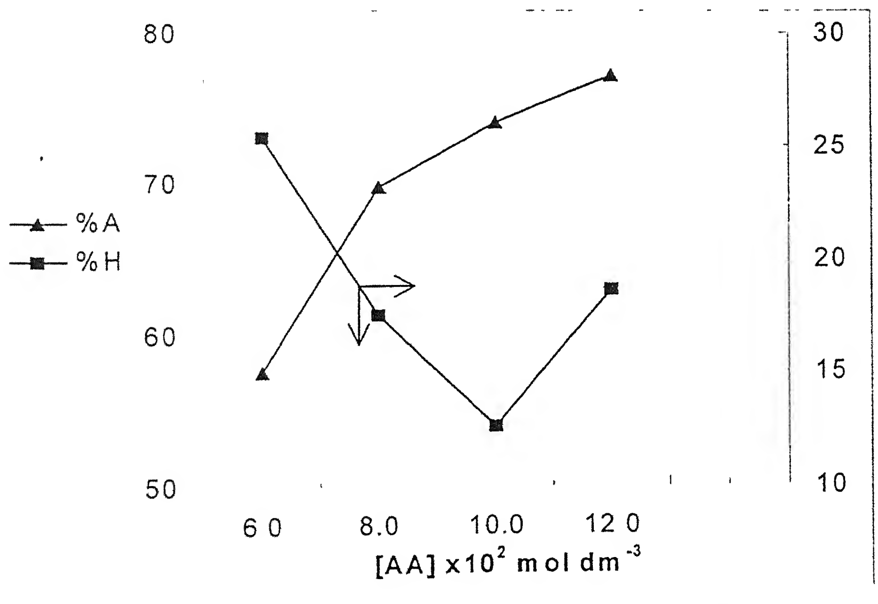


Figure 3 7 [PDP] = 2.0×10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0×10^{-3}mol dm^{-3}; [H^{+}] = 8.0×10^{-2} mol dm^{-3}; [Dextran] = 2.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

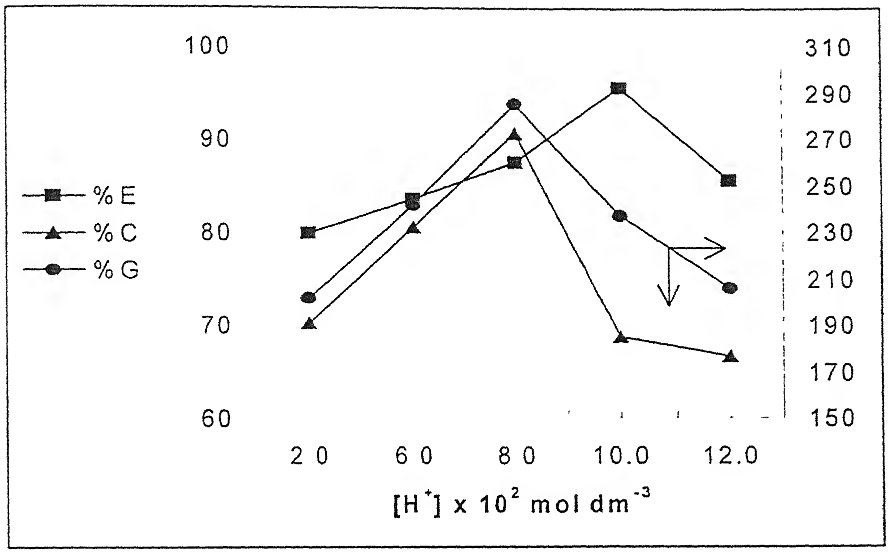


Figure 3.8 [PDP] = 2 0×10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0 ×10^{-3}mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3}; [Dextran] = 2 0 g. dm^{-3}; Time = 120 min. ; Temp = 35°C.

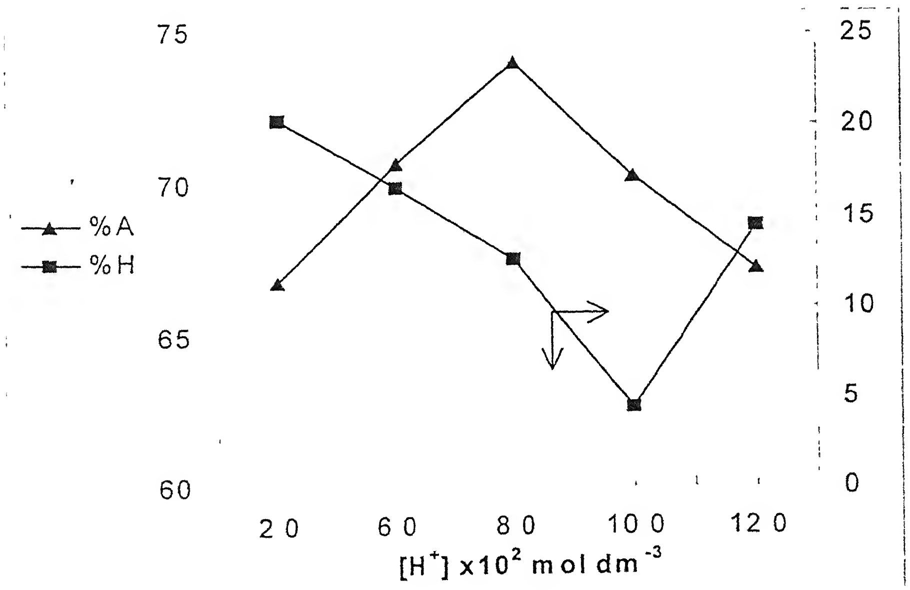


Figure 3.9 [PDP] = 2.0×10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0 ×10^{-3}mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3}, [Dextran] = 2.0 g. dm^{-3}; Time = 120 min. ; Temp.= 35°C.

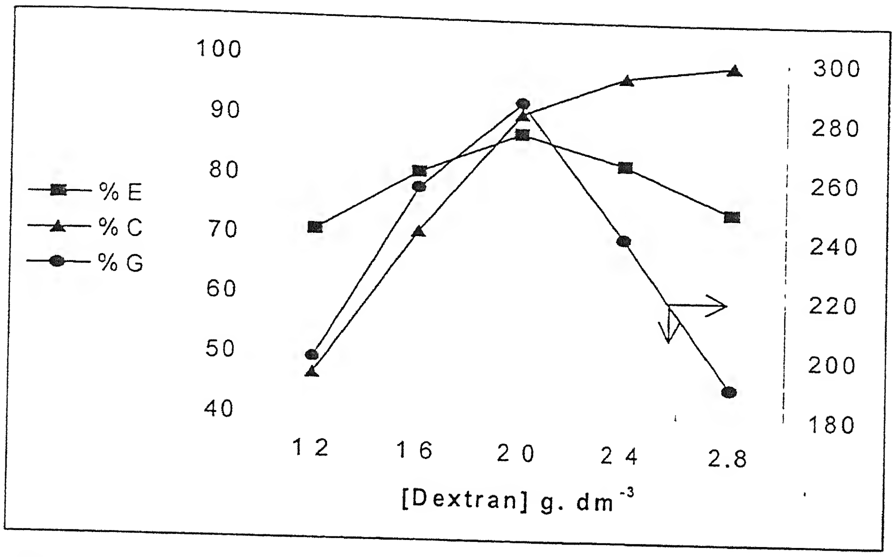


Figure 3 10 [PDP] = 2.0×10^{-2} mol dm^{-3}; [Ag^+] = 5.0×10^{-3}mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3}; [H^+] = 8.0×10^{-2} mol dm^{-3}; Time = 120 min. ; Temp.= 35°C.

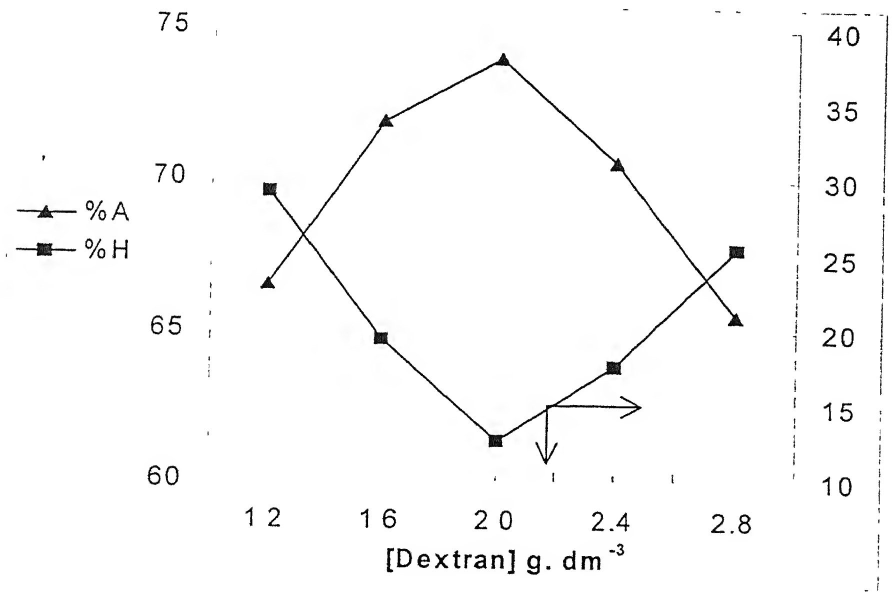


Figure 3.11 [PDP] = 2.0×10^{-2} mol dm^{-3}; [Ag^+] = 5.0×10^{-3}mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3}; [H^+] = 8.0×10^{-2} mol dm^{-3}, Time = 120 min. ; Temp.= 35°C.

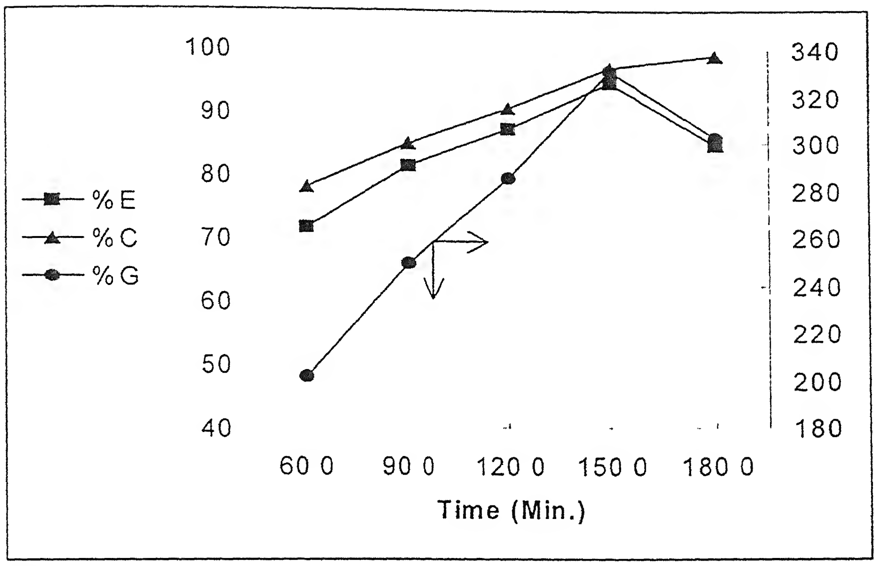


Figure 3 12 [PDP] = 2.0×10^{-2} mol dm^{-3}, [Ag^{+}] = 5.0 ×10^{-3}mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3}; [H^{+}] = 8.0 ×10^{-2} mol dm^{-3}, [Dextran]=2.0 g. dm^{-3} ; Temp.= 35°C.

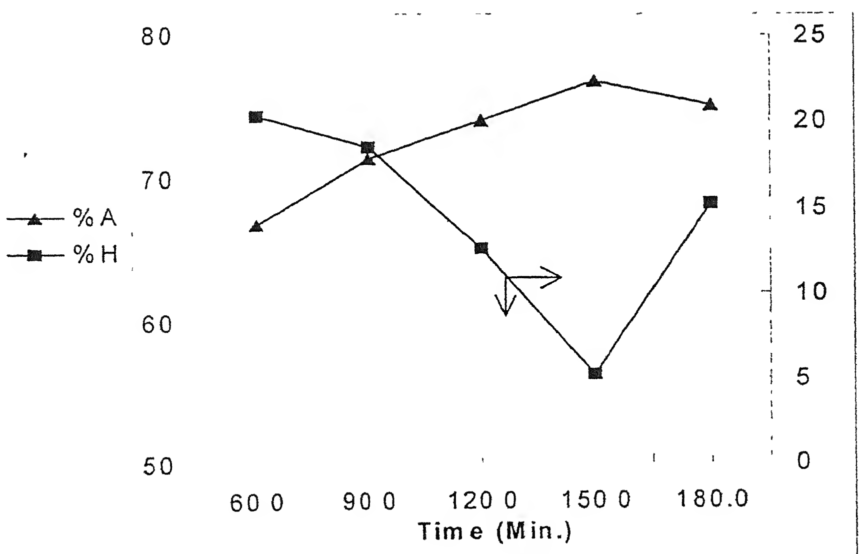


Figure 3.13 [PDP] = 2.0×10^{-2} mol dm^{-3}; [Ag^{+}] = 5.0 ×10^{-3}mol dm^{-3}; [AA] = 10.0×10^{-2} mol dm^{-3}; [H^{+}] = 8.0 ×10^{-2} mol dm^{-3}; [Dextran]=2.0 g. dm^{-3} ; Temp.= 35°C.

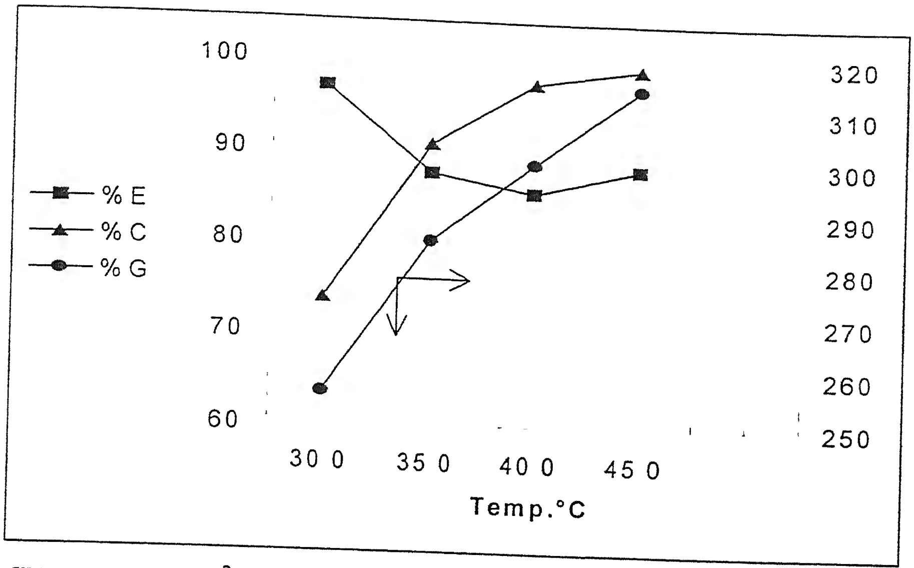


Figure 3 14 [PDP] = 2.0×10^{-2} mol dm^{-3}, $[Ag^+] = 5.0\times10^{-3}$ mol dm^{-3}, [AA] = 10.0×10^{-2} mol dm^{-3}: $[H^+] = 8.0\times10^{-2}$ mol dm^{-3}; [Dextran]=2.0 g. dm^{-3} ; Time=120 min.

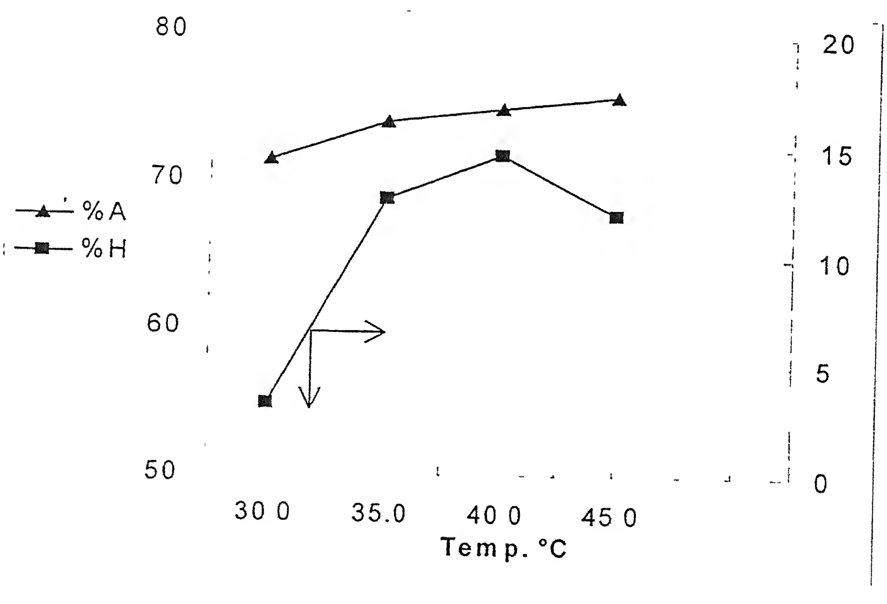


Figure 3.15 [PDP] = 2 0×10^{-2} mol dm^{-3}, $[Ag^+] = 5\ 0\times10^{-3}$ mol dm^{-3}, [AA] = 10.0×10^{-2} mol dm^{-3}. $[H^+] = 8.0\times10^{-2}$ mol dm^{-3}, [Dextran]=2.0 g. dm^{-3} ; Time=120 min.

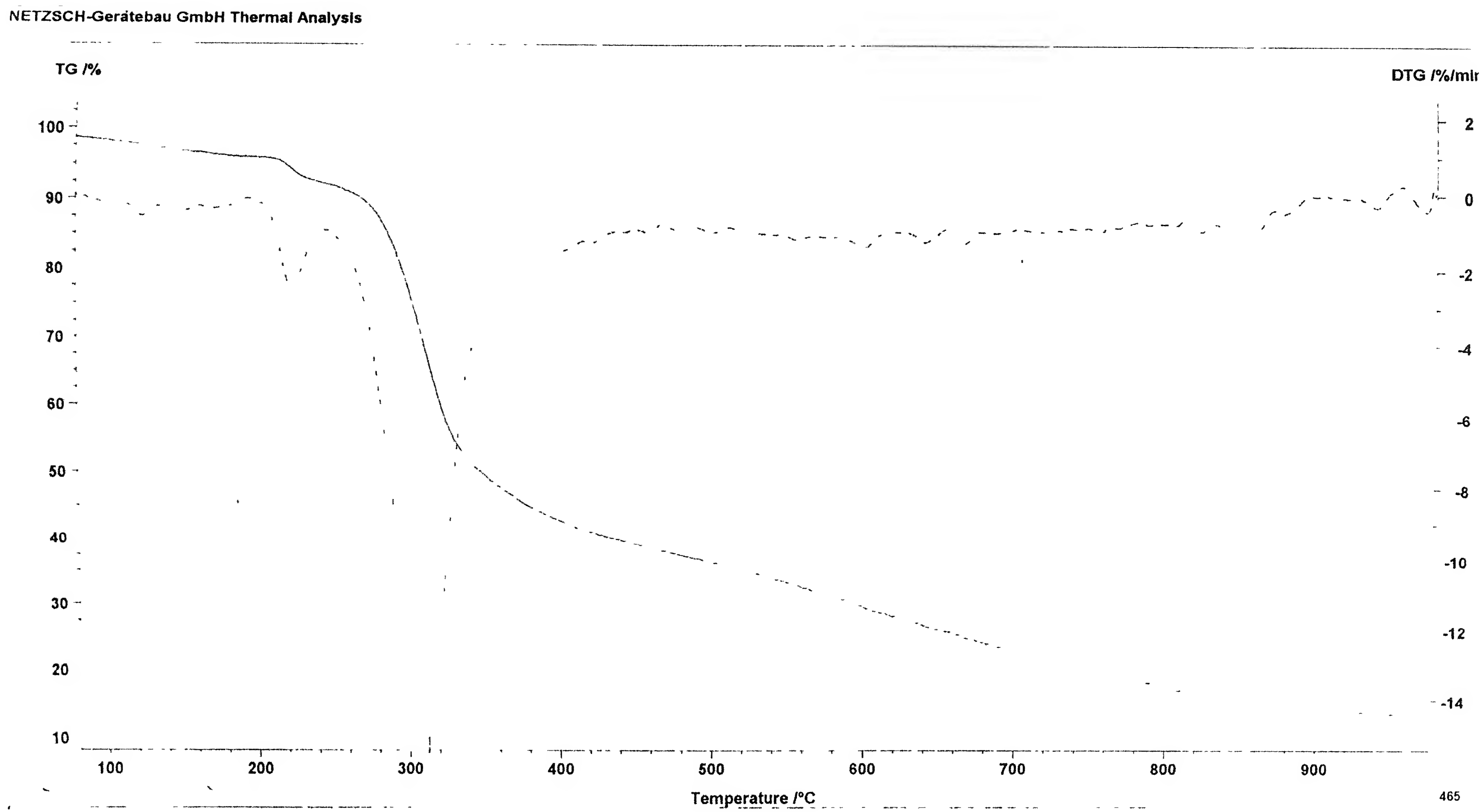


Fig 3.16 Thermogravimetric Trace of Dextran

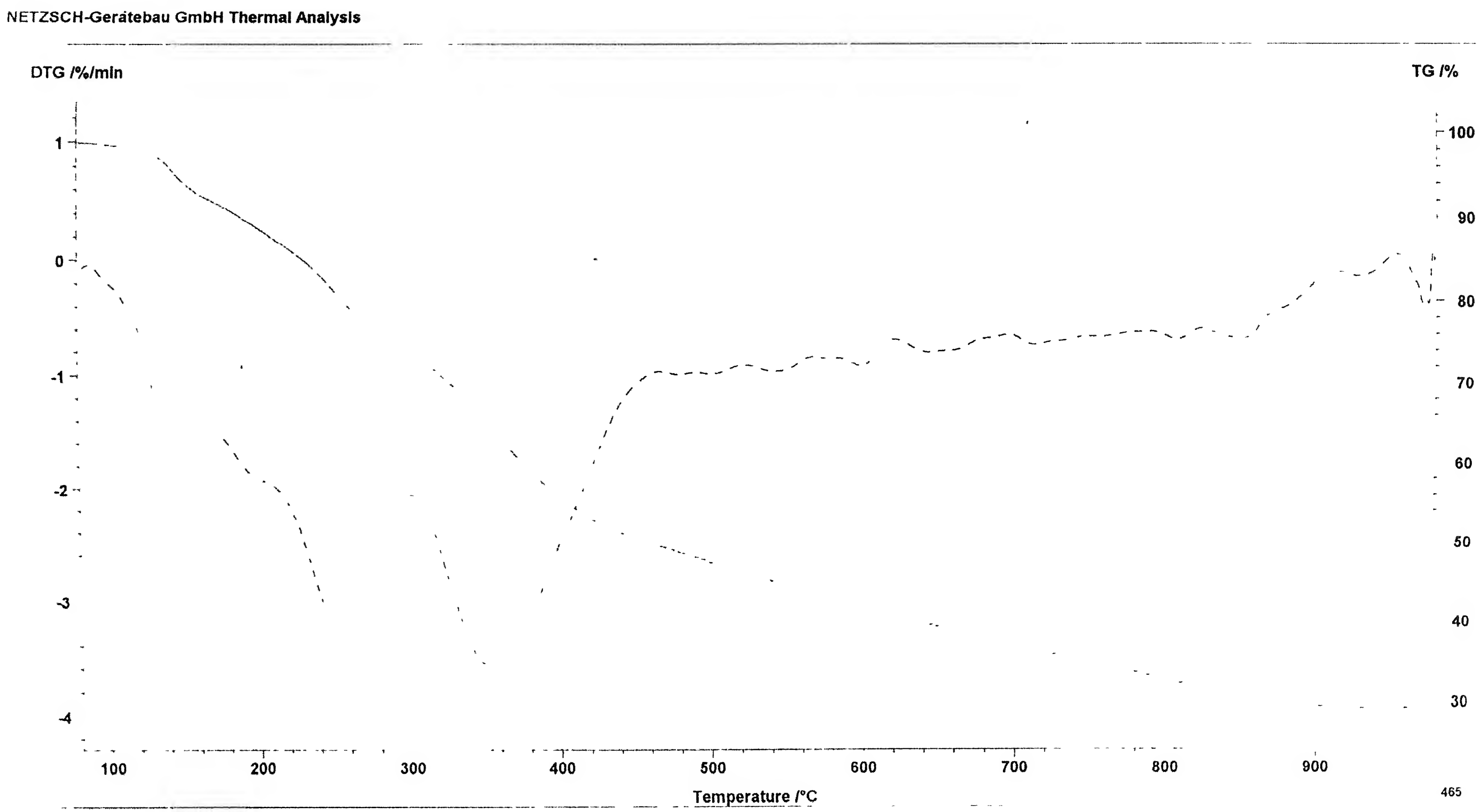
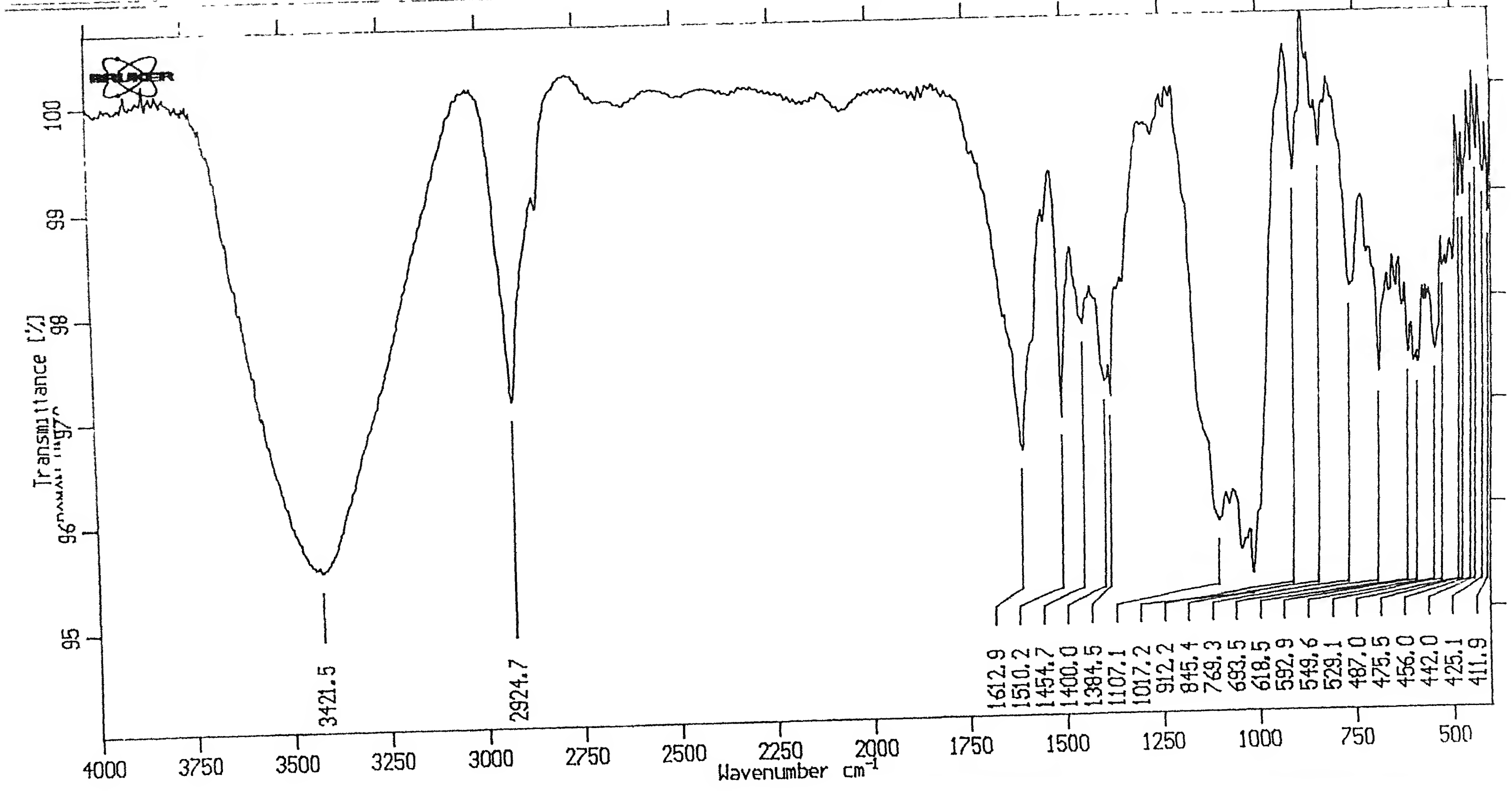


Fig. 3.17 : Thermogravimetric Trace of Dextran-g-acrylic acid



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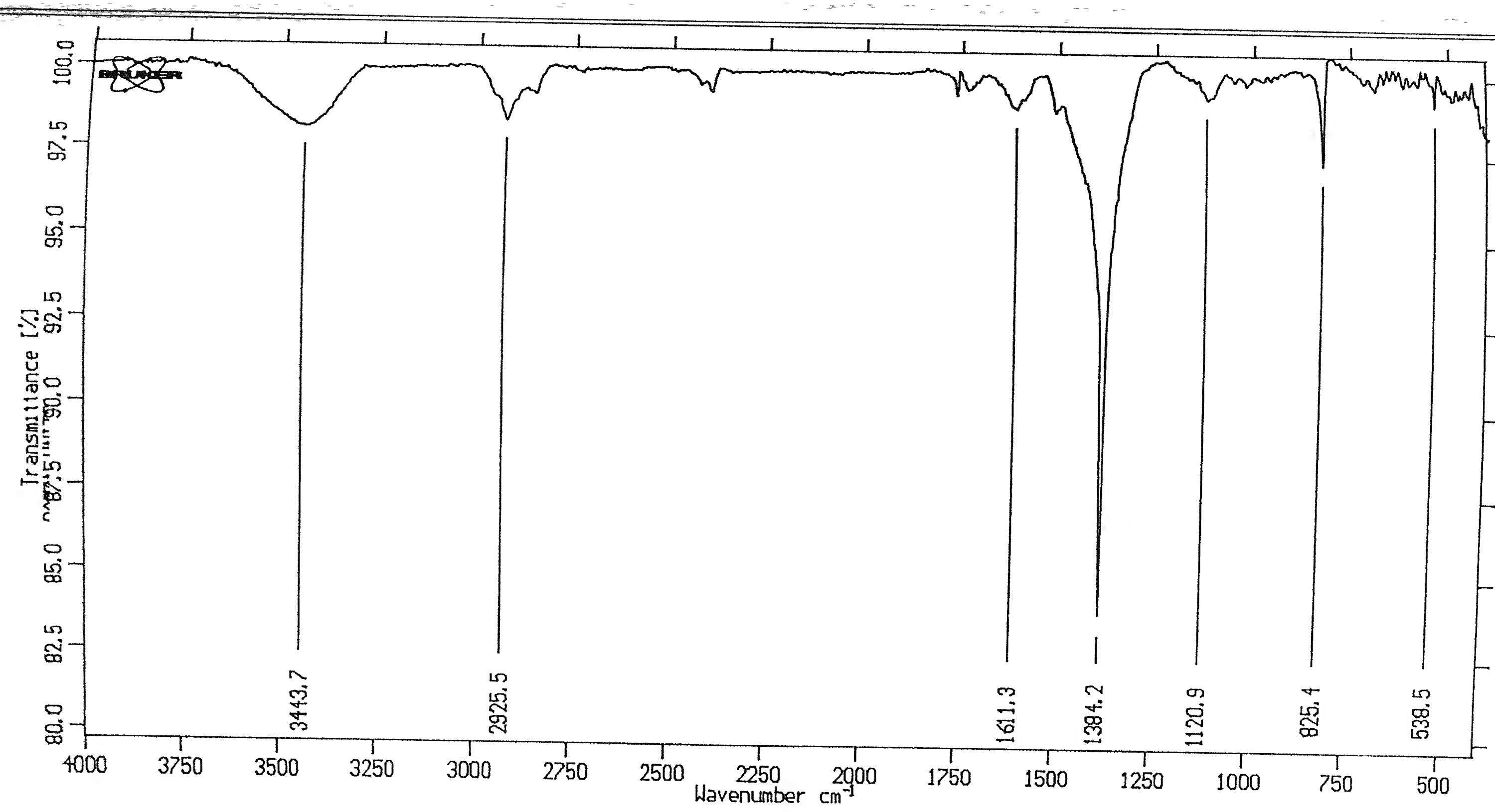
DATE : 27/ 2/2001	TECHNIQUE : KBr PELLET
TIME : 18: 0:18	USER : T.LALITHA
RESOLUTION : 4.0 cm-1	INSTRUMENT : IFS66V

Dextran



SPECTRUM : WORK.11 Dextran -g- Acrylic Acid
DATE : 27/ 2/2001
TIME : 17:58:16
RESOLUTION : 4.0 cm-1

SAMPLE : 466-R1
TECHNIQUE . KBr PELLET
USER : T.LALITHA
INSTRUMENT : IFS66V

REFERENCES

1 Tarr, H.L.A. and Hibbert, H.; Can. *J. Research* **5B,** 414 (1931).

2 Hehre. E J ; *Science* **93**, 237 (1941).

3 Larm. O., Lindberg. B. and Svensson, S.; *Carbohydr. Res* **20**, 39 (1971).

4 Walker, G.J. and Pulkownik, A.; *Carbohydr. Res.* **29**, 1 (1973).

5 Morris. E.R.; Rees, D.A.; Thom, D. and Welsh, E.J.; *J. Supramol. Struct.* **6**, 259 (1977).

6 Senti, F.R.; Hellman, N.N.; Ludwig, N.H.; Babcock, G.E.; Tobin, R.; Glass, C.A. and Lamberts, B.L.; *J Polym Sci.* **17**, 527 (1955).

7. Ebert, K.H. and Rupprecht, G.; *Makromol Chem.* **94**, 153 (1966).

8. Jeanes, A.; Haynes, W.C.; Wilham, C.A.; Rankin, J.C.; Melvin. E.H.; Austin, Marjorie; Cluskey, J.E.; Fisher, B.E.; Tsuchiya, H.M. and Rist, C.E.; *J. Am. Chem Soc.* **76**, 5041 (1954).

9. Wales, M.; Marshall, P.A. And Weissberg, S.G.; J. Polymer Sci. 10, 229 (1953); *Chem Abstr.* **47**, 6176 (1953)

10 Wales, M.; Marshall, P.A.; Rothman, S. and Weissberg, S.G.; Ann. N.Y. Acad Sci. 57, 353 (1953), *Chem Abstr.* **48**, 4286 (1954).

11. Senti, F.R.; Hellman, N.N.; Ludwig, N.H.; Babcock, G.E.; Tobin, R.; Glass, C.A. and Lamberts, B.L.; *J. Polymer Sci.* **17**, 527 (1955); *Chem. Abstr* **50**, 8292 (1958).

12. Wall, F.T and Childers, C.W.; *J. Am. Chem. Soc.* **75**, 3550 (1953).

13. Ogston. A.G. and Woods, E F.; *Nature* **171**, 221 (1953); *Chem. Abstr.* **47**, 4694 (1953)

14 Jeanes. A in Jeanes, A and Hodge, J. eds, *Physiological Effect of Food Carbohydrates, ACS Symp Ser. No.15, American Chemical Society*, Washington, D.C., **1975**, pp. 336-347.

15. Allen. A.W.; *U.S. Patent* 2,677,645 (1954); *Chem Abstr.* **48**, 902 (1954).

16. Toulmin, H.A. Jr.: *U.S Patent* **2,749,277** (1956).

17. Russell, K.L. and Nelson, M.F. Jr.; *U.S. Patent* 2,779,708 (1957).; *Chem Abstr* **51**. 6095 (1957).

18. Colgate-Palmolive Co., *British Patent* 753,757 **(1956)**.

19. Toulmin, H.A. Jr.; *U.S. Patent* 2731,349 **(1956)**, *Chem. Abstr.* **50**, 12348 **(1956)**.

20. Patricia Q. Peake; *U.S. Patent* 2,764,843 **(1956)**; *Chem. Abstr.* **51**, 2224 (1957).

21. Geoghegan, M.J.; *Trans. 4th Intern Congr. Soil Sci., Amsterdam* 1,198: 4,103 **(1950)**; *Proc. Soc Appl. Bacteriol.* P.77 **(1997)**, *Chem. Abstr.* **46**, 2217 (1952).

22. Martin, J.P. and Aldrich, D.G.; *Soil Sci Soc. Am.; Proc.* **19**, 50 (1955); *Chem. Abstr.* **49**, 10556 (1955).

23. Novak, L.J.; Wilt, E.E. and Hiler, M.J.; *J. Agr. Food Chem.* **3**, 1028 (1955).

24 Novak, L.J.; *U.S. Patent* 2,756,134 **(1956)**; *Chem. Abstr.* **50**, 16013 (1956).

25 Deniston, G.L.: *U.S Patent* 2,725,303 **(1955)**; *Chem. Abstr.* **50**, 3786 (1956).

26 Fowler. F.L.; Buckland. I.K.: Brauns, F and Hibbert, H; *Can Research* **15B**, 486 (1937); *Chem. Abstr.* **32,** 2088 (1938)

27 Waldie, W.A. and Bersuder, J.E.; *U.S Patent* 2,344,190 **(1944)**; *Chem Abstr* **38**, 3298 (1944).

28. Grönwall, A.J T., Ingelman, B.G.A. and Mosimann, H.; *Upsala Lakareforen Forh.* **50**, 397 (1945); *Chem. Abstr.* **41**, 5213 (1947).

29. Grönwall, A.J.T : Ingelman, B.G.A. and Mosimann, H.; *Swedish Patent* 118,014 **(1947)**; *Chem Abstr.* **41**, 6023 (1947).

30. Grönwall, A.J.T ; Ingelman, B.G.A. and Mosimann, H.; *British Patent* 603, 571 **(1948)**.

31. Ricketts, C.R.; *Biochem J.* **51**, 129 (1952).

32. Payne, H.G ; Baker, P.J.Jr.; *Am J Med Technol.* **19**, 219 (1953); *Chem Abstr* **48**, 2261 (1954).

33 Stahly, G.L. and Carlson, W.W.; *U S Patent* 2,203,703 **(1940)**; *Chem Abstr.* **34**, 6944 (1940).

34 Stahly, G.L. and Carlson, W.W.; *U S. Patent* 2,203,704 (1940), *Chem. Abstr.* **34**, 6944 (1940).

35. Stahly, G.L. and Carlson, W.W.; *U.S. Patent* 2,229,941 **(1941)**; *Chem. Abstr.* **35**, 3012 (1941).

36. Toulmin, H.A. Jr.; *U.S. Patent* 2,734,828 **(1956)**; *Chem. Abstr.* **50,** 7479 (1956).

37. Deniston, G.L.; *U.S. Patent* 2,706,690 **(1953)**; *Chem. Abstr.* **49,** 10635 (1955).

38. Deniston, G.L.; *U S. Patent* 2,731,369 **(1956)**; *Chem. Abstr.* **50,** 8221 (1956).

39. Hultin, E. and Nordström; *Swedish Patent* 146,220**(1954)**, *Chem. Abstr* **49**, 1286 (1955).

40 Inoue, Kazuhero; Susaki. Hiroshi, Ikeda. Masahiro; Kuga, Hiroshi; Kumazawa. Eiji: Togo, Akiko (Daiichi Pharmaceutical Co. Ltd.; Drug Delivery System Institute Ltd.; Inoue, Kazuhiro; Susaki, Hiroshi, Ikeda, Masahiro: Kuga. Hiroshi; Kumazawa, Eiji; Togo, Akiko, Japan) *PCT Int Appl* W09746,260 *(Cl A61 K47/48)*, **11 Dec. 1997**, *J.P Appl.* 96/144,421. 6 **Jun 1996;** 82 pp. (Japan).

41. Greenwald, H L Luskin. L.K.S.; in Davidson, R.L. ed.; *'Handbook of Water Soluble Gums and Resins'*, McGraw Hill, New York, Chapt. 17, pp 1-19 (**1980**).

42. Bayazeed, A.; Elzairy, M.R. and Hebeish, A; *Starke* **41(6)**, 233 (1989).

43 Date, M ; Sumiya. T.; Tanka, K., *Ger Offen DE* 4,127,814 *(Cl. C08F8/04)*, **(1992)**.

44. Date. M.; Sumiya, T.; Tanka, K.; *Ger Offen DE* 4,127,889 *(Cl. C08F6/04)*, (1992).

45. Hebeish. A.; Elzairy, M.R.; Rafie, H.M.; Higazy, A. and Elsisy, E.; *Starke* **42(3)**, 98 (1991).

46. Cao, A.B.; Song, R.; Wang, C.; *Hua Xueshejie*, **33(11)**, 19(1992).

47. Mostafa. Kh. M.; *J Appl. Polym Sci* **56(2)**, 263-9 (1995).

48. Miyata, N.; Sakata, I.; *Jpn. Kokkai Tokkyo Koho JP* 6397,612 [8897, 612] *(Cl CO8. 251/00)*. **(1988)**.

49. Wilmarth, W.K. and Haim, A.; in *'Peroxide Reaction Mechanism*, Ed. J.O. Edwards; Wiley Inter science, New York, 175 **(1962)**.

50. Morgan. L.B.; *Trans Faraday Soc.* **42**,169 (1946).

51. King, C.V. and Steinbach, O F.; *J. Am. Chem. Soc.;* **52**, 4779 (1930).

52. Sorum. C.H. and Edwards. J.O.; *Ibid*, **74**, 1204 (1957).

53. Creases I.I. and Edweards J.O.; *Top Phosphorous Chem.;* **7**,379 (1972).

54 Hariharan. S S. and Meenakashi, A; *J Polym. Sci Polym. Lett Ed* **15,** 1 (1977)

55 Nayak, P.L., Lenka, S. and Dhal, A.K.; *J. Makromol. Chem. Rapid Commun.* **1,** 13 (1980).

56 Lenka, S. and Dhal, A.K., *Eur Polym J* **18,** 343 (1982).

57. Lenka, S., Nayak, P.L. and Dhal, A.K. *J Polym Sci.*; *Polym. Chem. Ed.* **19,** 211 (1981).

58 Pradhan, A.K.; Pati, N.C. and Nayaka, P.L.; *J. Macromol Sci. Chem. A* **18(3),** 395 (1982).

59. Nayak, P.L.; Lenka, S. and Mishra, M.K.; *J. Makromol Sci. Chem.* **16(4),** 843 (1981).

60. Lenka, S.; Nayak, P L. and Roy, S.; *J Macromol. Sci. Chem.* **A20,** 823 (1983).

61. Nayak, P.L.; Lenka, S. and Mishra, M.K.; *J. Appl. Polym. Sci.* **26,** 733 (1981).

CHAPTER-IV

Graft copolymerization of 2-Acrylamido-2-methyl-1-propanesulphonic acid (AMPS) onto carboxymethyl cellulose (Sodium salt)

1 *Structure, Chemical Composition, Properties and Uses of Carboxymethyl cellulose (sodium salt)*

2 *Graft copolymerization of 2-Acrylamido-2-methyl-1-propane sulphonic acid onto Carboxymethyl cellulose (sodium salt) by H_2O_2/Fe^{2+} Redox pair.*

1. STRUCTURE, CHEMICAL COMPOSITION, PROPERTIES AND USES OF CARBOXYMETHYL CELLULOSE (SODIUM SALT)

Sodium carboxymethyl cellulose a water soluble cellulose ether is manufactured by reacting sodium monochloroacetate with alkali cellulose Its ability to suspend solids and control the viscosity of aqueous solutions and to form strong, tough films has accounted for the rapid industrial growth of this gum. Sodium carboxymethyl cellulose was first used as a substitute for natural gums, but has since developed new markets based on its own properties. Currently, large volumes of this cellulose derivative are employed in paper, textile processing, detergents, drilling fluids and protective coatings

It is believed that each of the several companies engaged in manufacturing sodium carboxymethylcellulose employs different techniques to accomplish the reaction. Only one of these companies has disclosed its process[1]. Essentially, this consists of concurrently spraying aqueous sodium hydroxide and monochloro acetic acid onto powdered cellulose as it passes slowly through a revolving drum. The resulting mixture is aged to complete the reaction, oven dried and packed. The reaction that occurs can be represented as follows:

$$R_{cell}(OH)_3 + ClCH_2COONa + NaOH \rightarrow R_{cell}(OH)_2\, OCH_2\, COONa + NaCl + H_2O$$

The structure of sodium carboxymethylcellulose has been shown in fig. 4.1

PROPERTIES:

The properties of sodium carboxymethylcellulose can be controlled by varying the uniformity of substitution, the degree of substitution (D.S.) and the degree of polymerization (D.P.). The most common substitution range is between 0.4 and 0.8. Water solubility is achieved with a degree of substitution greater than 0.45. The D.P. for most commercial types ranges from 500 to 2000[2].

1. Rheology:

Solution of small molecules in water, oil, organic solvents and other liquids, which follow the same simple law of flow as does water, are called Newtonian liquids Solutions of sodium carboxymethylcellulose are non-Newtonian. There are two types of non-Newtonian behaviour exhibited by these solutions, pseudoplasticity and thixopopy[3,4] All sodium carboxymethylcellulose solutions are pseudoplastic. This means that if the viscosity of a solution is measured using a large applied force, which causes a high velocity of flow, the apparent viscosity is less than that of the same solution determined with a smaller force and a slower rate of flow. The phenomenon of thexotropy manifests itself as an increase in apparent viscosity when the solution remains at rest for a period of time The different flow characteristics of sodium carboxymethylcellulose solutions are of practical value in determining the type of gum required for a specific purpose.

2. *Viscosity:*

Sodium carboxymethylcellulose forms viscous solution. Sodium carboxymethylcellulose solution can be most readily prepared when (i) the gum concentration is low, (ii) the water is heated and (iii) vigorous agitation is applied. A smooth, clear solution of sodium carboxymethylcellulose can be obtained by passing the water solution through a homogenizer, viscolizer, or colloid mill. The high shear thus applied provides more complete molecular dispersion, which results in improved smoothness and solution clarity. The viscosity can be measured with the help of rotational viscometer

Viscosities of sodium carboxymethylcellulose solutions become lower with increasing temperature, but as the temperature drops, the viscosity rises to its original level[5]. In the presence of salts, there is an excess of cations, which prevents the rise in viscosity at low concentrations of sodium carboxymethylcellulose [6].

3. *Gelation:*

Gelation of sodium carboxymethylcellulose solutions by polyvalent cations can be controlled and used to advantage in cases in which a dry firm gel is desired. Ferric phosphate and basic aluminium acetate are two compounds, which can be used to control gelation The addition of 10-25% of either of these salts results in the formation of a firm gel in 1-5 hr The firmness of the gel is controlled by the concentrations of the gum and the salts and by the viscosity grade of the gum. An increase in the acidity or temperature increases the rate of gel formation; addition of phosphate, acetate, citrate and tartrate anions reduces it.

4. *Films:*

Water solutions of sodium carboxymethylcellulose can be evaporated to form clear films, which have excellent physical properties[7]. If the surface of a sodium carboxymethylcellulose film is moistened, it will soften, become tacky and adhere to another film when the two are pressed together. By applying this simple technique, it is possible to seal films to form pouches or bags.

USES:

Generally speaking, sodium carboxymethylcellulose is useful in applications in which hydrophilic colloids are indicated. The basic properties that enhance its commercial value are its abilities to thicken water, suspend solids in aqueous media, stabilize emulsions, and absorb moisture from films. These properties can be, and have been utilized in widely divergent applications[8].

1. *Paper:*

The grease-resistant, film-forming characteristics of sodium carboxymethylcellulose have made it a useful additive for paper and paperboard products. It can be used alone or in conjunction with starch on the size press[9] to give

increased dry strength properties[10] and improved surface characteristics

Sodium carboxymethylcellulose can be economically and successfully applied at the calendar stack[11] to increase dry strength and wax pick, decrease porosity, impart greater oil and grease resistance[12] and improve surface and gloss ink printing characteristics.

2. *Adhesiveness:*

The film forming ability, easy solubility in cold water and specific adhesion to a variety of surfaces make sodium carboxymethylcellulose an excellent adhesive. Since it is readily water- soluble, can be removed easily with a wet sponge and possesses no wet tack, it has found extensive use as a non-staining wall paper[13,14] and billboard adhesive.

3. *Textiles:*

Sodium carboxymethylcellulose has received considerable attention in the textile industry because of its ready solubility, excellent film forming characteristics and negligible biological, oxygen demand[15]. It has been particularly useful as a warp size for yarns and filaments. In many finishing plants, starch-desizing operations have resulted in stream pollution The use of sodium carboxymethylcellulose has eliminated, or at least markedly reduced this problem.

4. *Food:*

Chronic and acute toxicity studies have established the fact that cellulose gum is physiologically inert[16,17]. As a stabilizer for ice cream[18,19] sherbets [20,21] and other frozen confections[22], its water-retaining abilities prevent synerisis in icings, meringues[22], jellius[23], pie fillings[24] and puddings[25]. It increases volume and prolongs freshness of cakes and other backed goods[26] and is effective as a protective colloid in flavour emulsions and salad dressing[27]

See References On Page No. 106-108

Modified Sodium Carboxymethylcellulose and its Uses:

Many modifications of sodium carboxymethylcellulose have been prepared and reported in the literature One of the method of modifying it is graft copolymerization The graft copolymerization of cellulose and its derivatives with hydrophilic monomers has received considerable attention during the past decades as a convenient way of introducing ionizable or other polar groups into the cellulose backbone[28] These graft copolymers are widely applied in many industries such as papermaking, textiles, washing and environment protection.

When a mineral acid is added to a sodium carboxymethylcellulose solution, the free acid carboxymethyl cellulose is formed. The free acid can also be formed by removing cations from the solution with suitable ion-exchange resins. By this method a salt free, stable water dispersion of the acid form of carboxymethyl cellulose can be prepared This dispersion can be used to form water-insoluble films. This property is valuable in applications such as inks and shoe polishes. The graft copolymers of sodium carboxymethylcellulose with acrylamide and dimethylamininoethyl methylacrylate have been prepared[29]. These graft copolymers have the potential of being used in drilling mud and has the properties of filtrate loss controllability and inhibit clay swelling

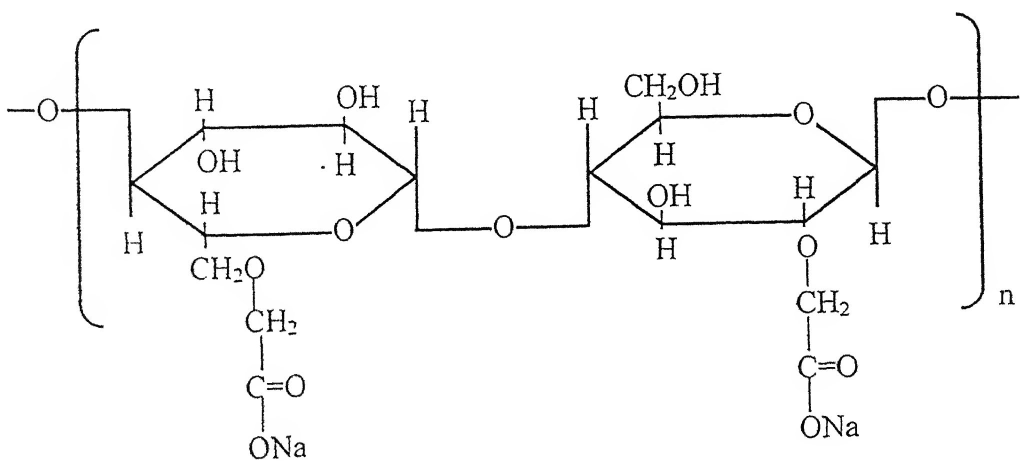


Fig. 4.1: Structure of Carboxymethylcellulose (Sodium Salt)

2. GRAFT COPOLYMERIZATION OF AMPS ONTO CARBOXYMETHYLCELLULOSE (SODIUM SALT) BY H_2O_2/Fe^{2+} REDOX PAIR:

Graft copolymerization of vinyl monomers onto natural and synthetic polymers is a fascinating field of research with unlimited potential application for industrial production of various materials[30-33] The grafting can be expected to add new properties associated with the side chains without drastically changing the basic properties of the natural polymer. These studies have been aimed at modifying various properties such as stereoregularity, hygroscopicity, thermal stability antistatic properties etc. Therefore the aim of this study is to graft suitable vinyl monomer onto sodium carboxymethylcellulose.

2-Arcylamido-2-methyl-1-propanesulphonic acid is characterized by its hydrophilicity and ionic character. Consequently, it has been used to prepare high swelling capacity polymer hydrogels[34] and its copolymers with some vinyl monomers such as acrylamide, methyl methacrylate and dimethylaminoethyl acrylate have been reported[35 36]

H_2O_2-Fe (II) system known as Fenton's reagent[37] is a very efficient redox system. It is known that hydroxyl radical ($OH^{\bullet}$) is generated by the reaction between Fe(II) and H_2O_2[38].

EXPERIMENTAL:

Material:

2-Acrylamido-2-methyl-1-propanesulphonic acid (Sigma) was used as such. H_2O_2 was diluted to desired concentration and its strength has been found titrametically. Carboxymethyl cellulose-sodium salt, (BDH) and ferrous sulphate (E Merck) were used as such. For hydrogen ions, H_2SO_4 (E. Merck) of desired concentration was used.

Procedure for Grafting:

For each experiment sodium carboxymethylcellulose solution was prepared by adding desired amount of sodium carboxymethylcellulose to 50ml of triple distilled water in a reactor The reaction was carried under nitrogen atmosphere at constant temperature A calculated amount of AMPS, ferrous sulphate and sulphuric acid solutions were added The stream of nitrogen gas was allowed to pass through the solution in reactor and H_2O_2 solution for half an hour. The reaction was initiated by the addition of H_2O_2 solution for half an hour. The reaction was initiated by the addition of H_2O_2. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into water methanol mixture. The precipitate was separated dried and weighed

RESULT AND DISCUSSION:

The graft copolymer has been characterized according to Fanta's definitions as discussed earlier. The effect of H_2O_2, Fe^{2+}, H^+, AMPS and sodium carboxymethylcellulose concentration as well as time and temperature on grafting parameters have been studied.

Effect of Hydrogen Peroxide Concentration:

The grafting reactions has been conducted by varying the concentration of H_2O_2 from 10.0×10^{-2} to 25×10^{-2} mol dm^{-3} (Table 4.1). The grafting ratio, add on and conversion increase with H_2O_2 concentration (10.0×10^{-2} to 15.0×10^{-2} mol dm^{-3}) (Fig. 4 3). The decrease in values of these parameters has been observed with further increase in H_2O_2 concentration. The decrease in the grafting ratio may be attributed to termination between growing chains and oligomeric vinyl radicals due to excess of free radicals.

Effect of Ferrous Ion Concentration:

The effect of ferrous ion has been studied by varying the concentration of ferrous sulphate from 0.5×10^{-2} to 6.0×10^{-2} mol dm^{-3} (Table 4.2). The grafting ratio, add on and conversion increase on increasing the concentration from 0.5×10^{-2} to 4.0×10^{-2} mol dm^{-3} and decrease with further increase in concentration (Fig. 4.2). The increase in grafting ratio with increase in Fe(II) concentration upto the cited range may be attributed to the increase in concentration of the free radicals produced by H_2O_2-Fe^{2+} redox pair resulting in the production of sodium carboxymethylcellulose radicals at the faster rate. The decrease in grafting ratio beyond 4.0×10^{-2} mol dm^{-3} may be attributed to a detrimental factor arising from the consumption of the OH° free radical (eq.)

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$$

Effect of AMPS Concentration:

The results of variation in AMPS concentration have been summarized in Table 4.3. It has been observed that grafting ratio and adds on increase with concentration of monomer. Conversion, however, decreases with monomer concentration (Fig. 4.4) The increase in grafting ratio may be attributed to the much ease accumulation of monomer at the close proximity of polymer backbone. The monomer molecules, which are at the immediate vicinity of the reaction sites, become acceptor of sodium carboxymethylcellulose radicals resulting in chain initiation and thereafter himself or herself become free radicals donor to the neighbouring molecule leading to lowering of termination.

Effect of Hydrogen Ion Concentration:

The effect of hydrogen ion concentration has been studied by varying the concentration of hydrogen ion from 0.01×10^{-2} to 10.0×10^{-2} mol dm^{-3} (Table 4.4). As

the hydrogen ion concentration is increased from 0.01x10^{-2} to 0.1x10^{-2} mol dm^{-3}, grafting ratio, add on and conversion increase, but decrease thereafter with increase in hydrogen ion concentration (Fig. 4.5). This could be interpreted in terms of an accelerated oxidation/reduction reaction at higher hydrogen ion concentration.

Effect of Carboxymethylcelluclose (Sodium Salt) Concentration:

The concentration of sodium carboxymethylcellulose has been varied from 0.4 to 1.6 g dm^{-3} to study the effect of sodium carboxymethylcellulose concentration on grafting parameters (Table 4.5). It has been observed that grafting ratio, add on and conversion decreases on increasing the sodium carboxymethylcellulose concentration (Figs. 4.6 & 4.7). The decrease in grafting ratio may be attributed to the fact that with increase in sodium carboxymethylcellulose concentration, its utilization ratio becomes smaller, as not enough AMPS reacted with sodium carboxymethylcellulose(39). Also the increased viscosity may hinder the movement of free radicals, as is evident from the decrease in total conversion of monomer.

Effect of Time Period:

Table 4.6 shows that grafting ratio, efficiency and add on increase as time period is increased from 60 to 90 min, but further increase in time period decreases these parameters (Figs. 4.8 & 4.9). This may be due to degeneration of growing grafted chains with increase in time period.

Effect of Temperature:

Table 4.7 reveals that grafting ratio, add on and conversion increase as temperature increases from 25°C to 30°C, but beyond this temperature, grafting decreases (Figs. 4.10 & 4.11). The increase in grafting ratio may be ascribed to the increased rate of diffusion of monomer onto backbone and increased rate of production of primary free radicals. The decrease in grafting ratio, add on and conversion may be attributed to the premature termination of growing grafted chains by excess of free radicals.

EVIDENCE OF GRAFTING:

I.R. Spectra:

On comparing the IR spectra of sodium carboxymethylcellulose and sodium carboxymethylcellulose-g-AMPS, following additional peaks in the spectra of sodium carboxymethylcellulose-g-AMPS has been observed.

Bands at 1641 cm^{-1} and 1620 cm^{-1} are due to C=O stretching vibrations (amide group) and N-H bending vibrations. The C-N stretching band of amide group appeared at 1451.1 cm^{-1} A broad medium band in 825.1-720.2 cm^{-1} region is due to out of plane N-H wagging These bands/peaks confirm the grafting of AMPS onto sodium carboxymethylcellulose

Thermal Degradation Behaviour of Carboxymethylcellulose (Sodium Salt).

The degradation of Sodium Carboxymethylcellulose started at about 135.3°C. The degradation occured in two stages i.e. from 135.3 to 283.1°C and from 283.1 to 385.2°C. About 40% weight loss occured between 200 and 400°C. The rate of weight loss increases on increasnig the temperature up to 285.0°C, but decreasing thereater. The polymer decomposition temperature (PDT), final decomposition temperture (FDT), T_{max} and integral procedural temperture (IPDT) were found to be 135.3, 385.2, 283.1 and 294.5°C respectively. Table 4.8 and 4.9 reveal that weight loss in the temperature range 400 to 700°C is almost constant. The char yield of 38% was obtained at 924°C (Fig. 4.12).

Thermal Degradation Behaviour of Carboxymethylcellulose (Sodium Salt)-g-AMPS:

Sodium Carboxymethylcellulose-g-AMPS graft copolymer has been obtained by grafting AMPS onto Sodium Carboxymethylcellulose using H_2O_2/Fe^{2+} redox pair

The graft copolymer began to degrade at about 180°C. However weight loss upto 114.8°C may be attributed to the absorbed water. The degradation appears to be two-stage process *i.e.* from 254.6 to 328°C and from 328 to 427°C. The T_{max}, polymer decomposition temperture (PDT) and final decomposition temperature (FDT) were found to be 254.6°C, 208.0°C and 427°C respectively. About 50% weight loss occured between 176 and 500°C and 26% char yield was obtained at 860°C The IPDT was found to be 344 4°C (Table 4 8 & Fig 4 13)

MECHANISM:

Hydroxyl radical is generated by the reaction of Fe(II) and H_2O_2[40].

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+}$$

The hydroxyl radical abstracts hydrogen atom from the sodium carboxymethylcellulose molecule, producing sodium carboxymethylcellulose free radical ($CO^{\bullet}$). The monomer molecules, which are in close vicinity of the reaction sites become acceptors of the sodium carboxymethylcellulose radicals resulting in the chain initiation and thereafter themselves become free radical donor to neighbouring molecules In this way grafted chains grow. These grafted chains terminate by coupling to give graft copolymer.

The reaction mechanism can be represented by the following steps:

$$COH + OH^{\bullet} \rightarrow CO^{\bullet} + H_2O$$

See References On Page No. 106-108

Initiation:

$$CO^{\bullet} + M \rightarrow COM_1^{\bullet}$$

Propagation:

$$COM_1^{\bullet} + M \rightarrow COM_2^{\bullet}$$

$$COM_2^{\bullet} + M \rightarrow COM_3^{\bullet}$$

. . . .

. . ..

.. . .

$$COM_{n-1}^{\bullet} + M \rightarrow COM_n^{\bullet}$$

Termination:

$$COM_n^{\bullet} + COM_m^{\bullet} \rightarrow \text{graft copolymer}$$

(COH = Sodium Carboxymethyl cellulose)

See References On Page No. 106-108

Table 4.1

Effect of H_2O_2

$[Fe^{2+}] = 1.0 \times 10^{-2}$ mol dm^{-3}; [AMPS] = 4.0×10^{-2} mol dm^{-3};
$[H^{+}] = 10.0 \times 10^{-4}$ mol dm^{-3}; [NaCMC] = 1.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S.N.	$[H_2O_2] \times 10^{2}$ mol dm^{-3}	% G	% A	% C
1	10 0	79.8	44.3	9.6
2	15 0	108 0	51 1	13.0
3	20.00	52.0	34.2	6.3
4.	25.0	50.2	33.4	6.0

Table 4.2

Effect of Ferrous Ion

$[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3}; [AMPS] = 4.0×10^{-2} mol dm^{-3};
$[H^{+}] = 10.0 \times 10^{-4}$ mol dm^{-3}; [NaCMC] = 1.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S.N.	$[Fe^{2+}] \times 10^{2}$ mol dm^{-3}	% G	% A	% C
1.	0.5	32.0	24.2	3.5
2.	1 0	52.0	34.2	6.3
3.	2.0	99 3	49.9	12.0
4	4.0	170.0	62.9	20.5
5.	6.0	72.5	42.0	8.8

See References On Page No. 106-108

Table 4.3

Effect of AMPS

$[Fe^{2+}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3};
$[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3}; [NaCMC] = 1.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S.N.	[AMPS]x10^2 mol dm^{-3}	% G	% A	% C
1.	2 0	32.7	24.7	7.9
2	4.0	52.0	34 2	6.3
3	6 0	55 2	35.6	4 4
4.	8.0	60.6	37.8	3.6

Table 4.4

Effect of Hydrogen Ion

$[Fe^{2+}] = 1.0 \times 10^{-2}$ mol dm^{-3}; [AMPS] = 4.0×10^{-2} mol dm^{-3};
$[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3}; [NaCMC] = 1.0 g dm^{-3};
Time = 120 min; Temp = 35°C.

S N.	[H$^+$]x10^2 mol dm^{-3}	% G	% A	% C
1.	0.01	34.0	25 4	4.1
2.	0.1	52.0	34.2	6.3
3.	1.0	16 0	13.8	2.0
4.	10.0	9.0	9.0	1.2

See References On Page No. 106-108

Table 4.5

Effect of Sodium Carboxymethylcellulose

$[Fe^{2+}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[AMPS] = 4.0 \times 10^{-2}$ mol dm^{-2};
$[H^{+}] = 10.0 \times 10^{-4}$ mol dm^{-3}; $[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3};
Time = 120 min; Temp = 35°C.

S.N.	[NaCMC] g dm^{-3}	% G	% A	% C
1.	0.4	210.0	67.7	10.1
2.	0.7	98.0	49.5	8.2
3.	1.0	52.0	34.2	6.3
4	1.3	45.1	31.1	7.0
5.	1.6	32.5	24.5	6.3

Table 4.6

Effect of Time Period

$[Fe^{2+}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[H_2O_2] = 20 \times 10^{-2}$ mol dm^{-3};
$[AMPS] = 4.0 \times 10^{-2}$ mol dm^{-3}; $[H^{+}] = 10.0 \times 10^{-4}$ mol dm^{-3};
$[NaCMC] = 1.0$ g dm^{-3}; Temp = 35°C.

S N.	Time (Min)	% G	% A	% C
1.	60	44.0	30.6	5.3
2.	90	82.2	45.1	9.9
3.	120	52.0	34.2	6.3
4.	150	43.0	30.0	5.2
5.	180	34.0	25.4	4.1

See References On Page No. 106-108

Table 4.7

Effect of Temperature

$[Fe^{2+}] = 1.0 \times 10^{-2}$ mol dm^{-3}; $[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3};
$[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3}; [AMPS] = 4.0×10^{-2} mol dm^{-3};
[NaCMC] = 1.0 g dm^{-3}; Time = 120 min;

S N	Temp °C	% G	% A	%C	%E	%H
1	25	57.6	36.5	6.9	100.0	0.0
2	30	61.7	38.1	7 4	100.0	0.0
3	35	52.0	34.2	6.3	100.0	0.0
4	40	49.0	32.8	5.9	100.0	0.0

Table 4.8

THERMOGRAVIMETRIC ANALYSIS OF GRAFT COPOLYMER

Sample Code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
G_1	135.3	385.2	283.2	294.5
G_2	208.0	427.0	254.6	344.4

Table 4.9

DECOMPOSITION TEMPERATURE (T°D)

Sample	T°D (°C) at following weight loss						
	10%	20%	30%	40%	50%	60%	70%
G_1	270.0	284.0	296.0	382.0	740.0	904.0	--
G_2	207.0	256.0	307.0	363.0	441.0	589.0	763.0

See References On Page No. 106-108

Table 4.10

DECOMPOSITION TEMPERATURE (T^oD)

Temp (°C)	Weight loss (%)	
	G_1	G_2
100	1 2	1 5
200	2.9	7.1
300	29.4	25.0
400	38.8	43.5
500	42.9	52.8
600	43.0	60.0
700	44.7	65.0
800	52.3	71.4

G_1 = Sodium Carboxymethylcellulose

G_2 = Sodium Carboxymethylcellulose-g-AMPS (H_2O_2/Fe^{2+})

See References On Page No. 106-108

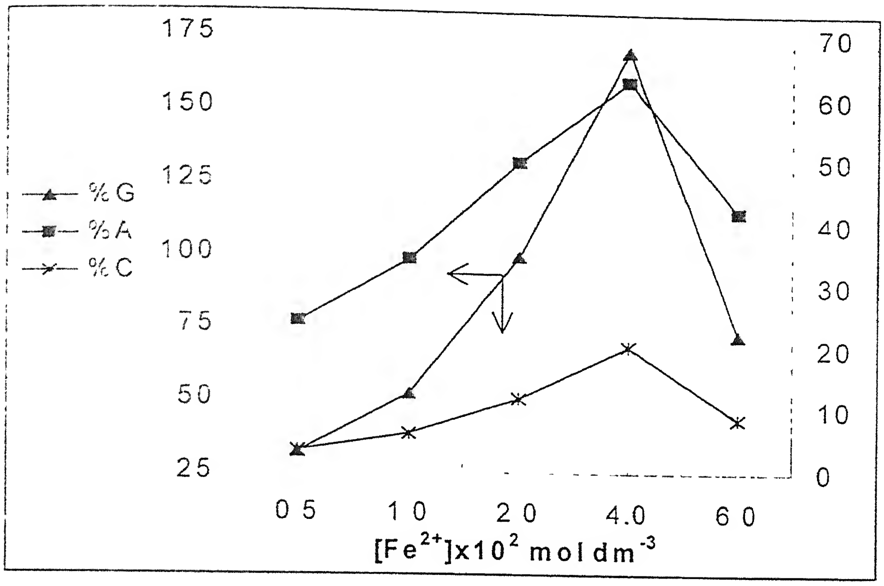


Figure 4.2 $[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3} ; [AMPS] = 4.0×10^{-2} mol dm^{-3} ; Temp. = 35°C; $[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3} ; [NaCMC] = 1.0 g. dm^{-3} ; Time = 120 min.

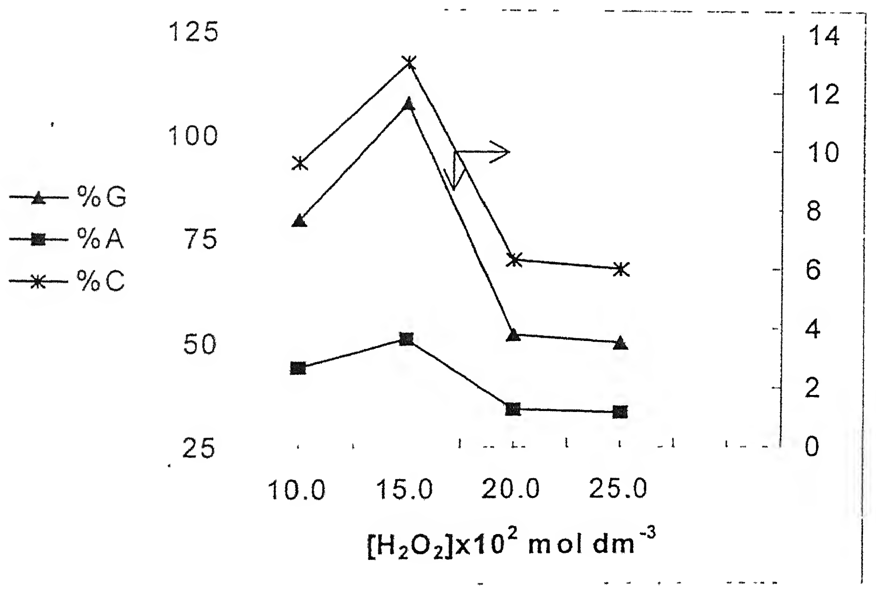


Figure 4.3 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; [AMPS] = 4.0×10^{-2} mol dm^{-3} ; Temp. = 35°C; $[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3} ; [NaCMC] = 1.0 g dm^{-3} ; Time = 120 min.

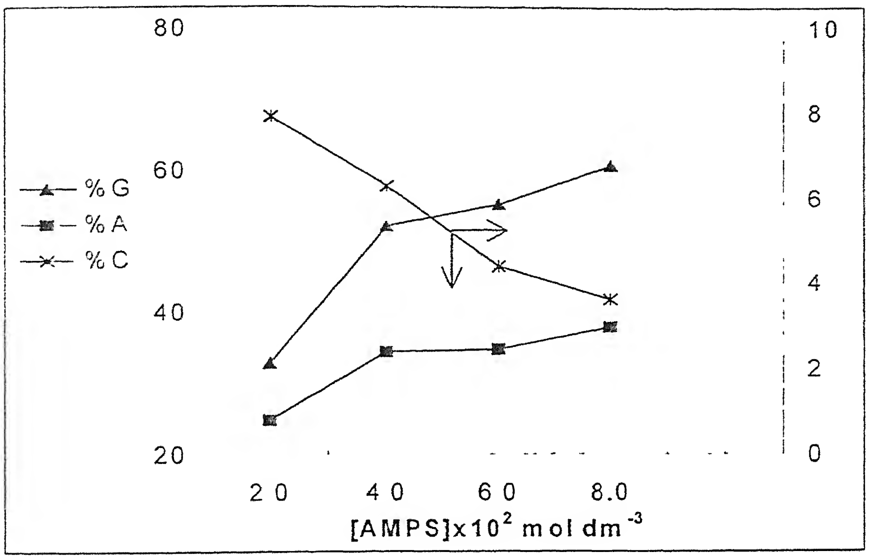


Figure 4.4 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; $[H_2O_2] = 20.0\times10^{-2}$ mol dm^{-3} ; Temp. = 35°C; $[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3} ; [NaCMC] = 1.0 g. dm^{-3} ; Time = 120 min.

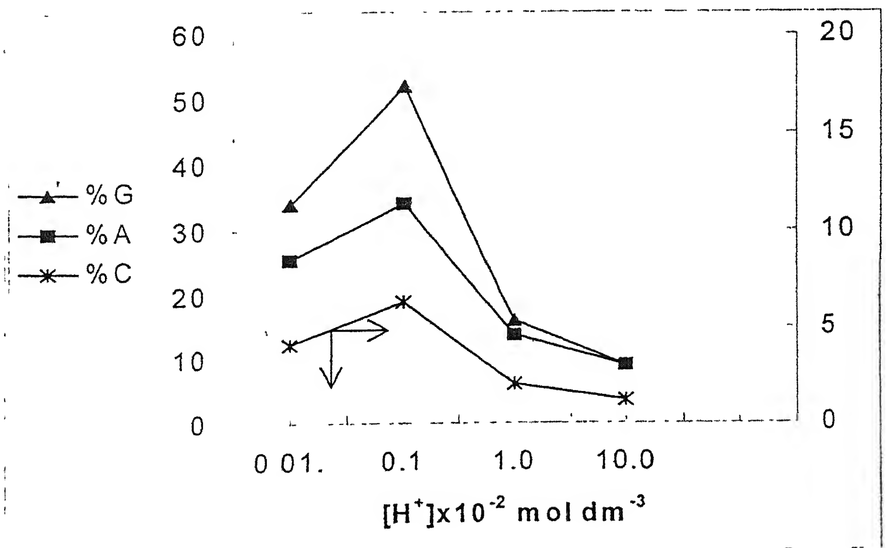


Figure 4.5 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; $[H_2O_2] = 20.0\times10^{-2}$ mol dm^{-3} ; Temp. = 35°C; $[AMPS] = 4.0 \times 10^{-2}$ mol dm^{-3} ; [NaCMC] = 1.0 g. dm^{-3} ; Time = 120 min.

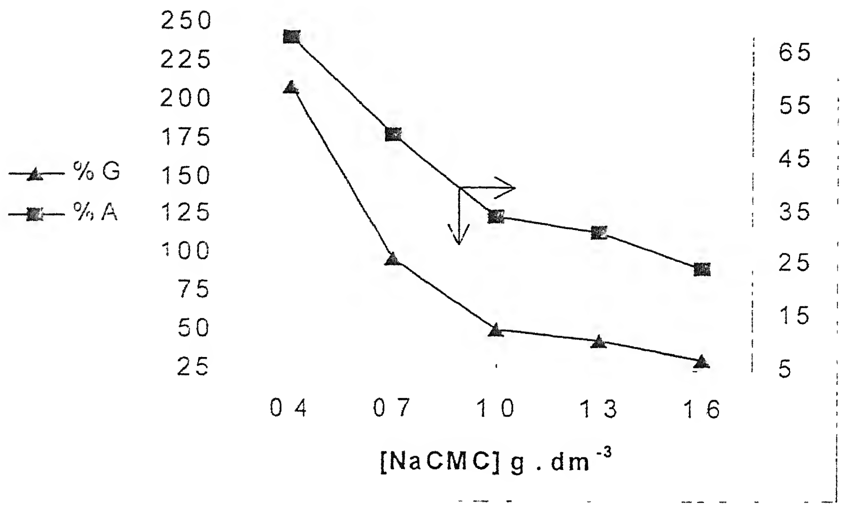


Figure 4.6 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} , $[H_2O_2] = 20\ 0 \times 10^{-2}$ mol dm^{-3} ; Temp. = 35°C; $[AMPS] = 4\ 0 \times 10^{-2}$ mol dm^{-3} ; $[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3} ; Time = 120 min.

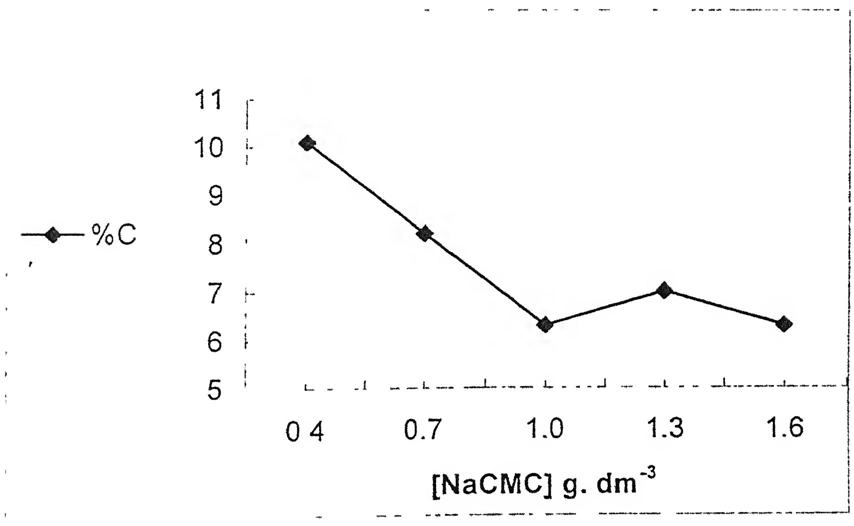


Figure 4.7 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; $[H_2O_2] = 20.0 \times 10^{-2}$ mol dm^{-3} ; Temp. = 35°C; $[AMPS] = 4.0 \times 10^{-2}$ mol dm^{-3} ; $[H^+] = 10.0 \times 10^{-4}$ mol dm^{-3} ; Time = 120 min.

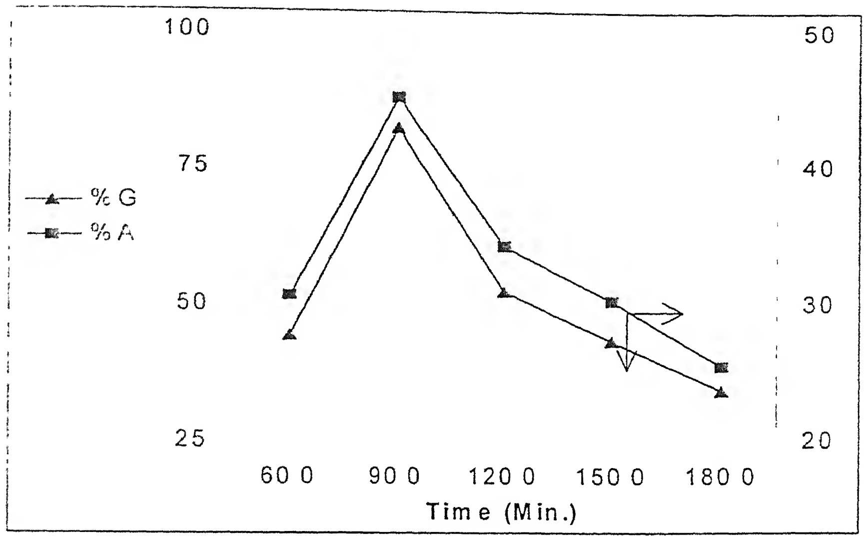


Figure 4.8 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; $[H_2O_2] = 20.0\times10^{-2}$ mol dm^{-3} ; Temp. = 35°C; [AMPS] = 4 0 $\times10^{-2}$ mol dm^{-3} ; $[H^+] = 10.0\times10^{-4}$ mol dm^{-3} ; [NaCMC] = 1.0 g dm^{-3} .

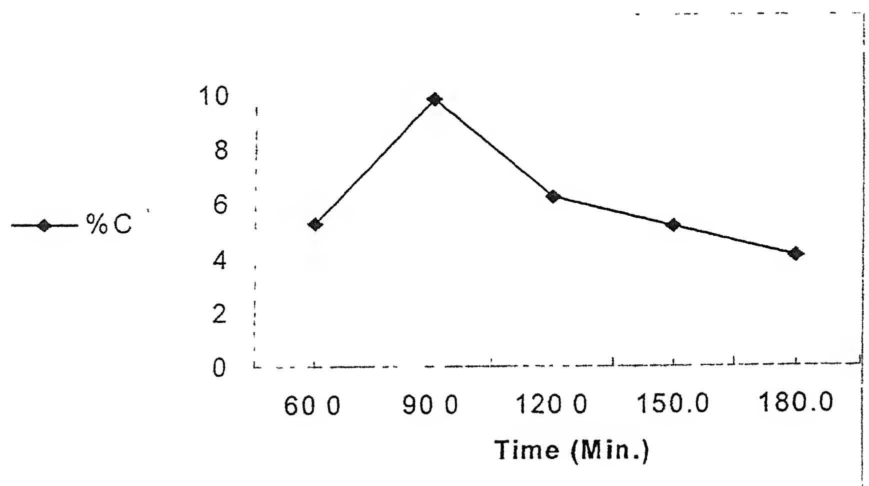


Figure 4.9 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; $[H_2O_2] = 20.0\times10^{-2}$ mol dm^{-3} ; Temp. = 35°C; [AMPS] = 4.0 $\times10^{-2}$ mol dm^{-3} ; $[H^+] = 10.0\times10^{-4}$ mol dm^{-3} ; [NaCMC] = 1.0 g dm^{-3} .

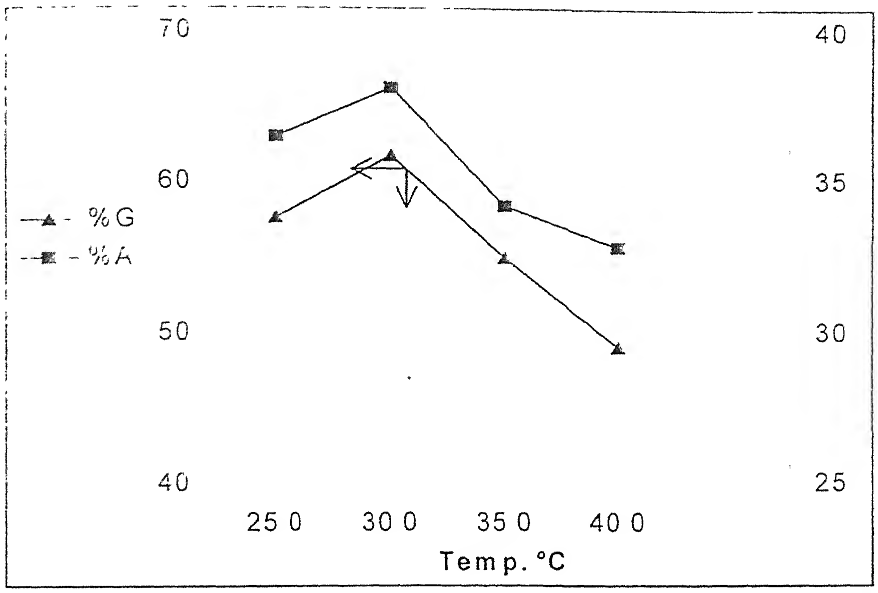


Figure 4.10 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} , $[H_2O_2] = 20.0\times10^{-2}$ mol dm^{-3} ; Time =120 min. [AMPS] = $4\ 0 \times 10^{-2}$ mol dm^{-3} , $[H^+] = 10.0\times10^{-4}$ mol dm^{-3} , [NaCMC] = 1.0 g dm^{-3} .

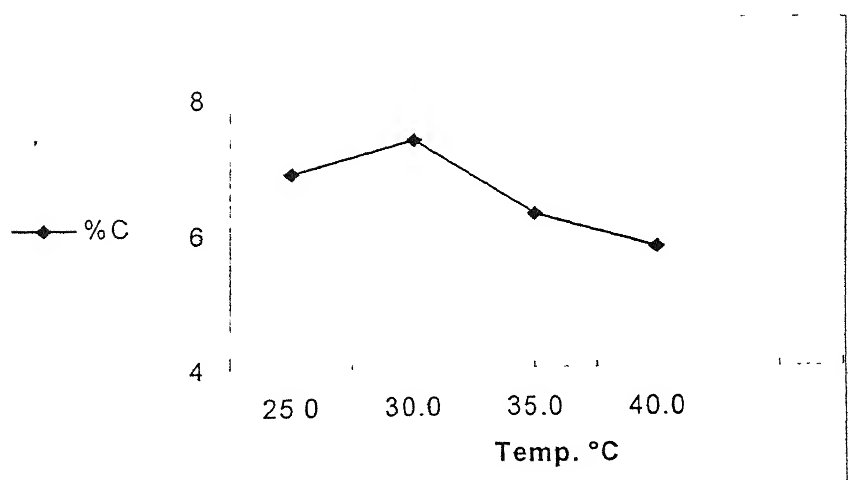


Figure 4.11 $[Fe^{2+}] = 10.0 \times 10^{-2}$ mol dm^{-3} ; $[H_2O_2] = 20.0\times10^{-2}$ mol dm^{-3} ; Time =120 min. [AMPS] = 4.0×10^{-2} mol dm^{-3} ; $[H^+] = 10.0\times10^{-4}$ mol dm^{-3} ; [NaCMC] = 1.0 g dm^{-3} .

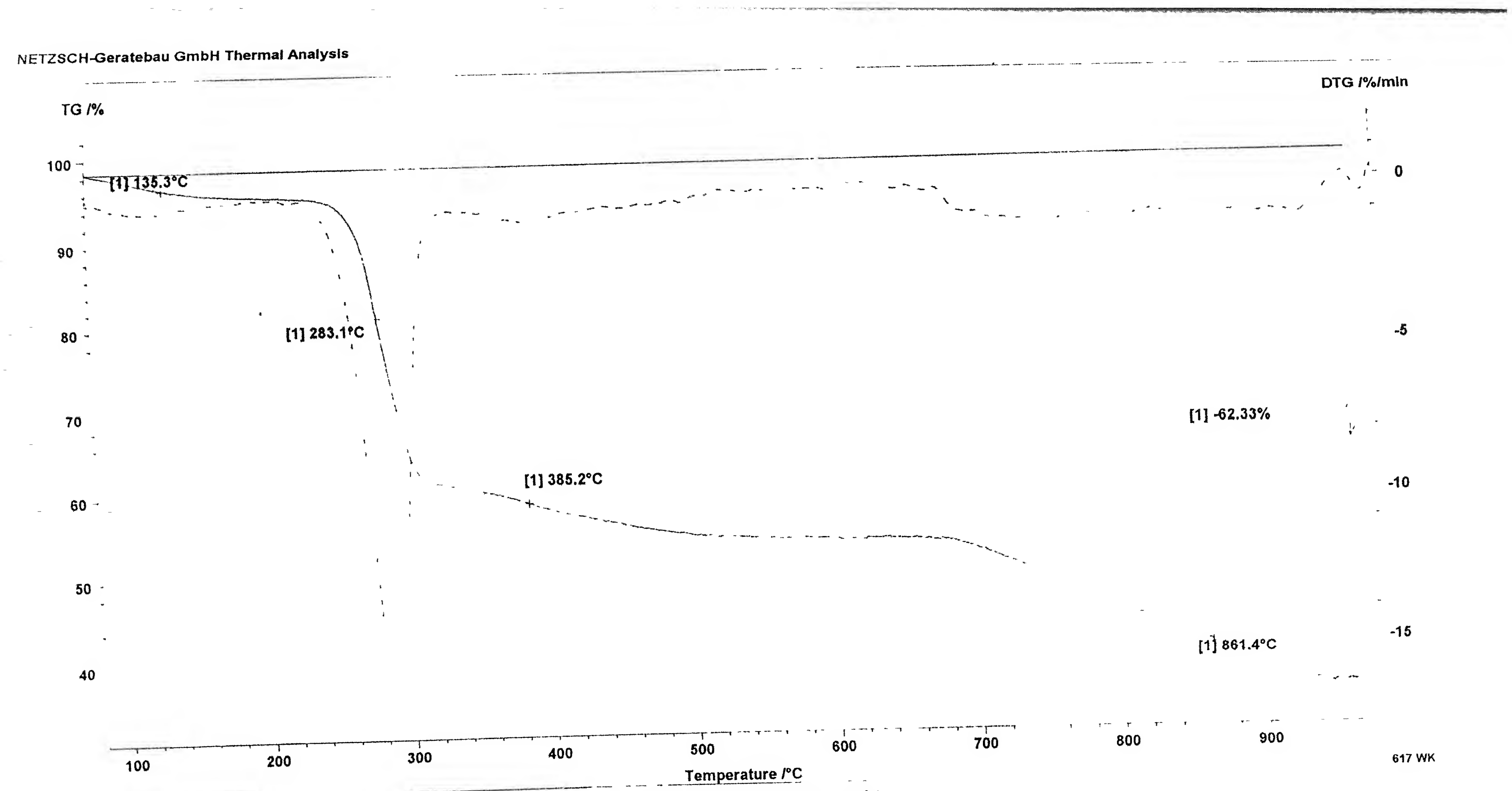


Fig 4.12 : Thermogravimetric Trace of Carboxymethylcellulose (sodium salt)

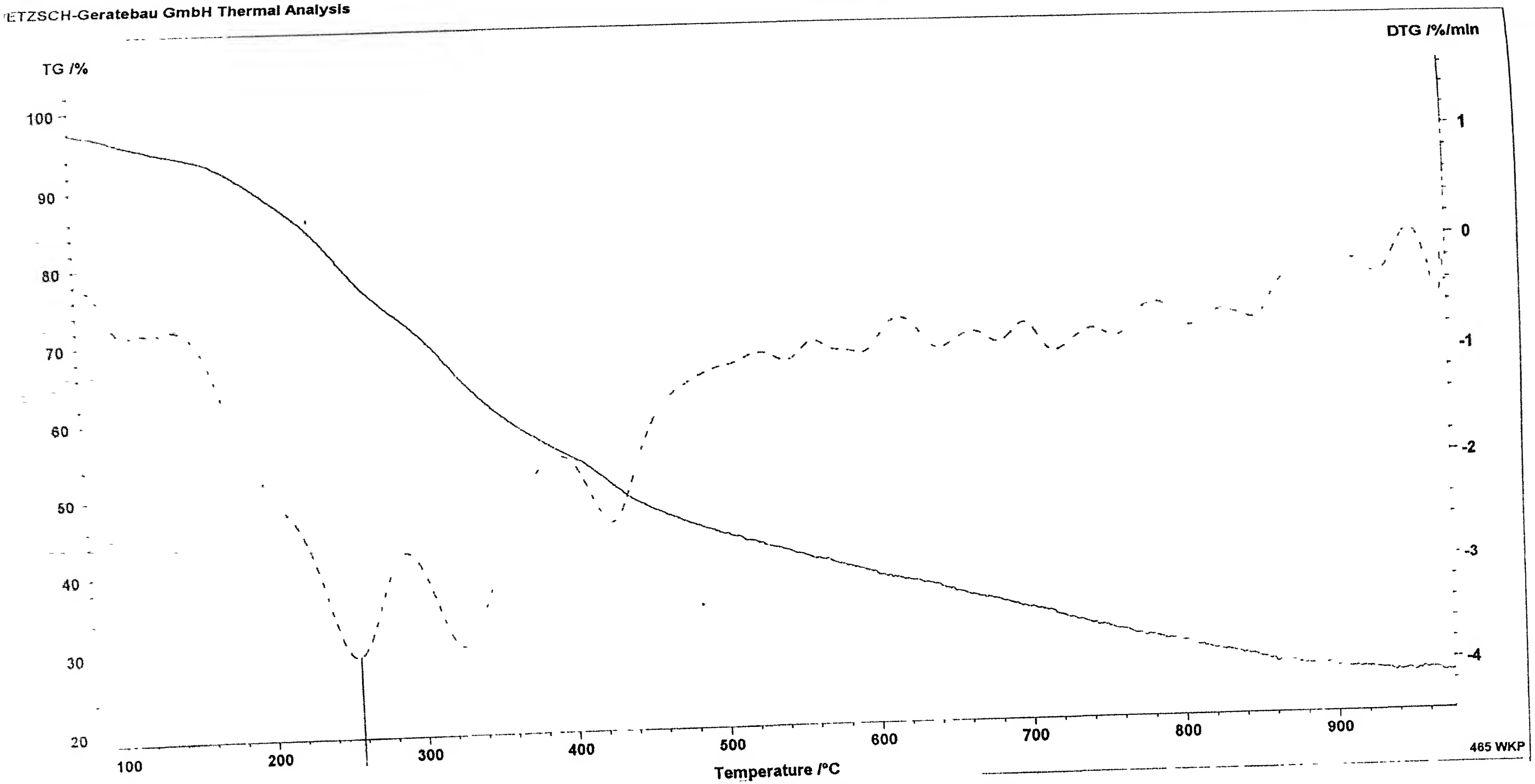
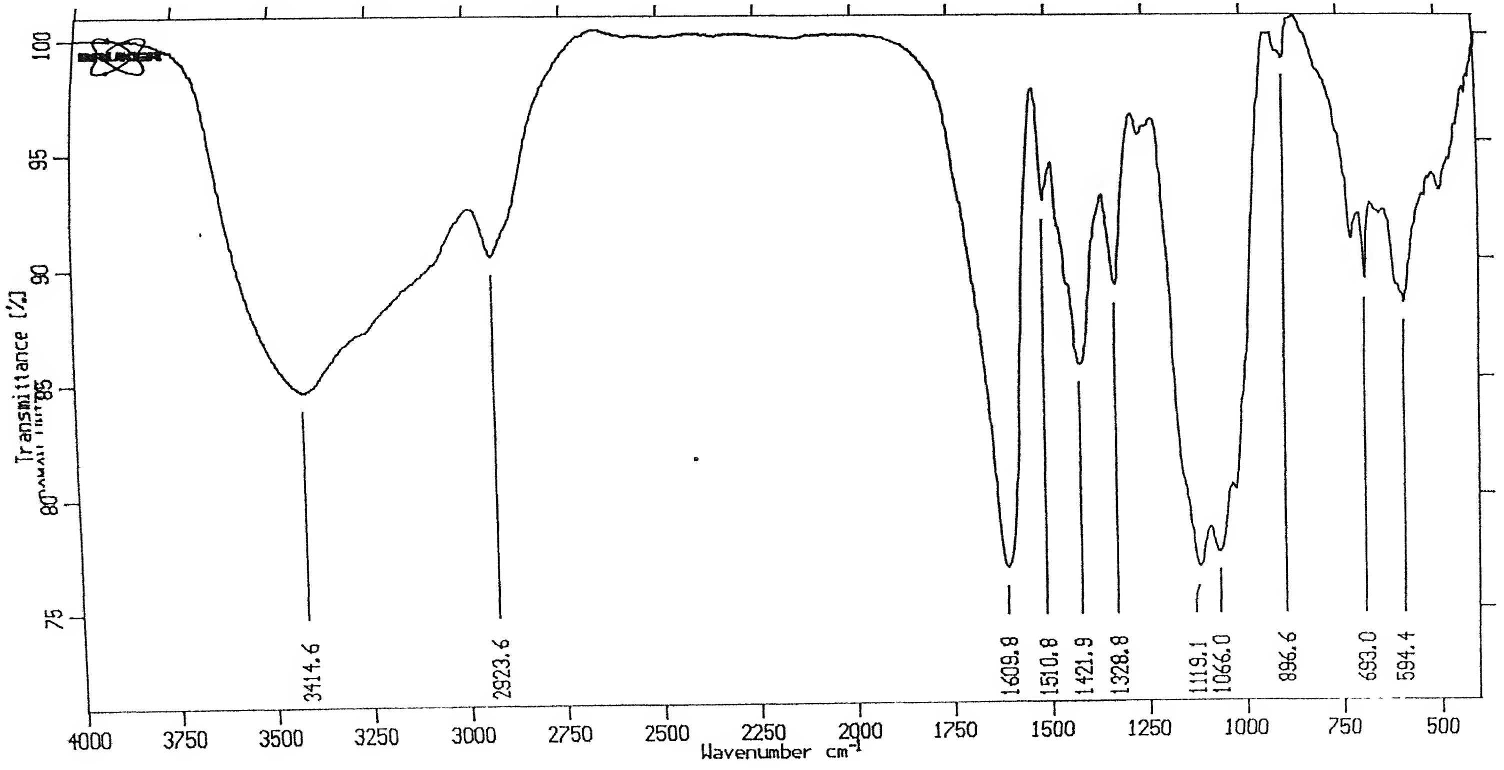


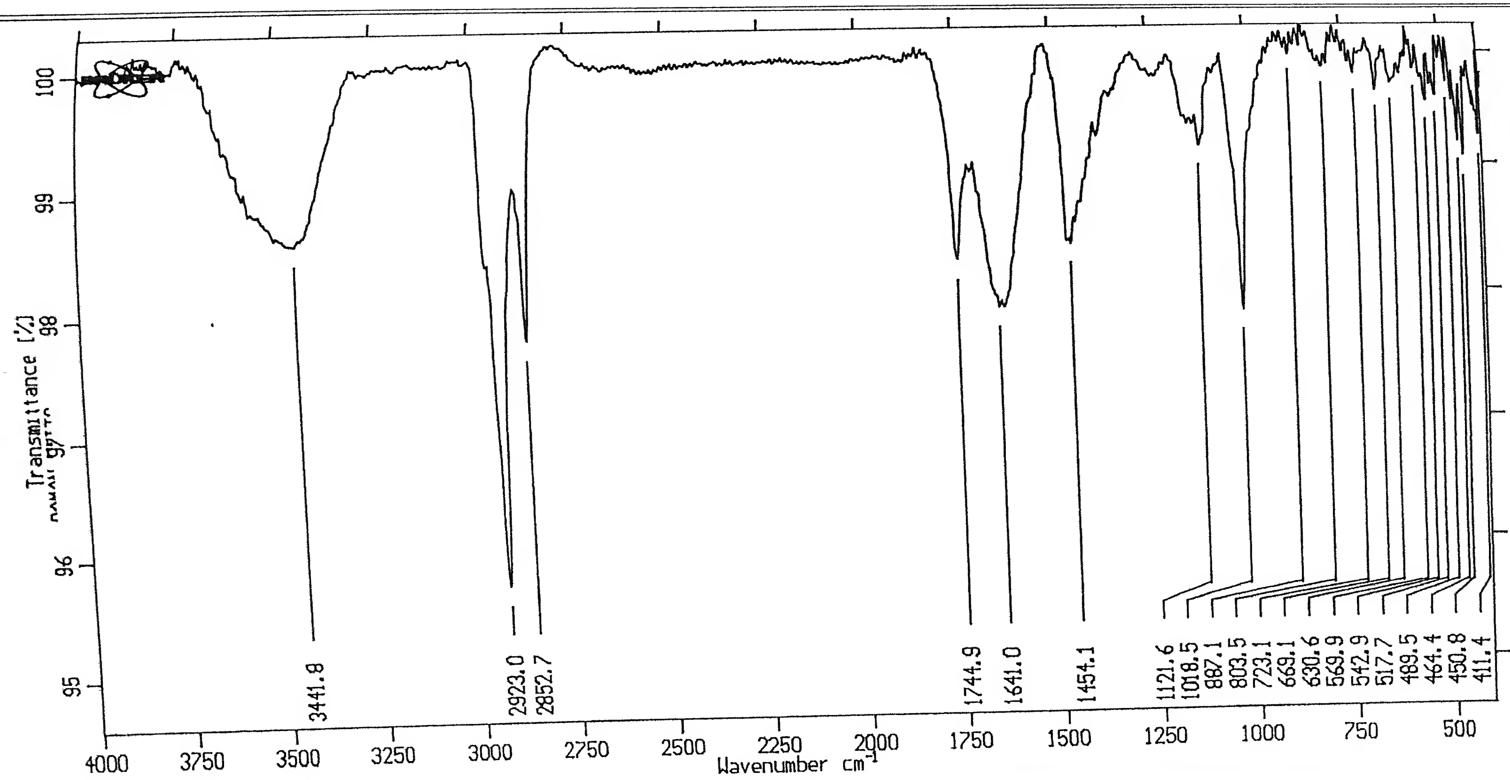
Fig. 4.13 : Thermogravimetric Trace of Carboxymethylcellulose (sodium salt)-g-AMPS



SPECTRUM : WORK.10
DATE : 27/ 2/2001
TIME : 17:53:55
RESOLUTION : 4.0 cm-1

Carboxymethyl cellulose (Sodium Salt)

SAMPLE : 466-Q2
TECHNIQUE : KBr PELLET
USER : T.LALITHA
INSTRUMENT : IFS66V



SPECTRUM : WORK.9
DATE : 27/ 2/2001
TIME : 17:51:54
RESOLUTION : 4.0 cm-1

Carboxymethyl cellulose (Sod. Salt) -g- AMPS.

SAMPLE : 466-Q1
TECHNIQUE : KBr PELLET
USER : T.LALITHA
INSTRUMENT : IFS66V

REFERENCES

1. Hader, R.N., Waldeck, W.F. and Smith, F.W.; *Ind Eng Chem.* **44**, 2803 (1952)

2. Timell, T.E., *Svensk Papperstiden* 56, 311 (1953).

3. Butts, E.H., Hudy, J.A. and Elliott, J.H.; *Ind Eng Chem.* 49, 94 (1957)

4. Ott, E.; and Ellicott, J.H.; *Makromol Chem* **18-19**, 353 (1956).

5. *'Properties and uses of Hercules Cellulose Gum. (CMC)'*, Hercules Powder Co., Wilmington, Del.

6. Akkerman, F.; Pals, D.T.F. and Hermans, J.J.; *Rec. Trav. Chem.* **71**, 56 (1952)

7. *'Properties and uses of Hercules Cellulose Gum (CMC),'* Hercules Powder Co. Wilmington, Del.

8. Hollabaugh, C.B., Burt, L.H. and Walsh, Anna, P.; *Ind. Eng. Chem.* 37, 943 (1945).

9. Horrey, Eleanor and Donna Price, *U.S. Patent* 2,572,932 **(1951)**; *Chem Abstr.* **46,** 1786 (1952).

10. Seymour, R.B. and Schroder, G.M., *U.S. Patent* 2,48,803 **(1949)**, *Chem Abstr.,* **44,** 3263 (1950).

11. Horrey, Eleanor, F.; *Paper Trade J.* **125, No.4,** 52 (1947).

12. Heller, H.F.; *Paper* **17, No.2**, 17 (1948).

13. Deney, H.J.; *U.S. Patent* 2,524,008 **(1950)**; *Chem. Abstr.* **45**, 4096 (1955).

14. Jenkins, R.H.; *Chem. Eng. News* **32**, 3310 (1959).

15. Dickerson, B.W., *Ind. Waste* **1,** 10 (1955).

16 Lehman, A.L., *Assoc. Food and Drug Oficials U.S. Quart. Bull.* 14, 82 (1950).

17. Shelanoski, H.A. and Clark, A.M.: *Food Research* **13**, 29 (1948).

18 Burt, L.H.: *U.S. Patent* 2548,865 **(1951)**; *Chem. Asbtr.* 45, 6320 (1951)

19 Julien, J.P., *Ice Cream Trade J.* **49, No.9**, 44 (1953).

20 Landers, M., *U.S. Patent* 2,423,600 **(1947)**; *Chem. Abstr.* 41, 5998 (1947)

21 Onderzoekinginstituut 'Research' N.V., *Dutch Patent* 73,644 **(1953)**; *Chem. Abstr.* 48, 6617 (1954).

22 Hollabaugh, C.B.; Burt, L.H. and Walsh, Anna, P.; *Ind. Eng. Chem.* 37, 943 (1945).

23 Berglund, D.T.; *Svensk Papperstidh* **51**, 555 (1948).

24. Anderson, E.E.; Esselen, W.B. and Fellers, C.R.; *J. Am. Dietet Assoc.* **29**, 770 (1953).

25 Hollabaugh, C.B.; Burt, L.H. and Walsh, Anna, P.; *Ind. Eng. Chem.* **37,** 943 (1945).

26. Schuurink, F.A.; *Dutch Patent* 59,870 (1947); *Chem. Abstr.* **41, 7014** (1997).

27. Hollabaugh, C.B.; Burt, L.H. and Walsh, Anna, P.; *Ind. Eng. Chem.* **37,** 943 (1945).

28. Zhang, Li-Ming; Taw Ye-Bang; *Macromol. Mater. Eng.,* **280/282,** 59-65 (2000).

29. Tan, Yebang; Zhang, Liming; Li, Zhuomie; *J. Appl. Polym. Sci.,* **69,** 879-885 (1998).

30. Gurnechaga, M.; Goni, I.; Valeri, M., Guzman, G.M.; *Polymer* **33 (15),** 3274 (1992).

31. Mah Soukel; Oh., Yoomnee; Yu Jaehyung; *Hanguk. Somyu. Konghakhoe Chi.* **31 (3)**, 179 (1994).

32. Sakamoto, M.; Hasuika, Hi; Itoh, M.; Ishizuka, Y.; Yoshida, K.; Watamoto, H.; Furuhata, K.; *Cellul Chem. Biochem. Mater Aspects* **391** (1993).

33. Varadarajan, P.V.; Shaikh, A.J.; Lokhande, H.T.; *Trends Carbohydr. Chem. Carbohydr. Conf.* **9th Jan 1993**, 147 (1995).

34. Kulicke, W.M.; Nottlemann, H.; Aggour, Y.A.; Elsabee, M.Z.; *Polym., Mat. Sci. Eng,* **61,** 393 (1989).

35. Aggour, Y.A.; *Polym. Deg. Stab.* **44,** 71 (1994).

36. Aggour, Y.A.; *Polym. Deg. Stab.* **45**, 273 (1994).

37. Walling, A.; *Acc. Chem. Res.* **8**, 125-131 (1975).

38. Jefcoate, Lindsay - Smith and Norman, *J Chem. Soc.* **B.** 1013 (1969); Brook, Castle, Lendray-Smith, Higgens and Morris, *J. Chem. Soc., Perkin Trans.* 2,687 (1982); Lai and Piette, *Tetrahedron Lett.* (1979).

39. Tan, Yebang; Zhang, Liming; Zhuomie, Li; *J. Appl. Polym. Sci.* 69, 879-885 (1948).

40. Jefcoate, Lindray-Smith and Norman, *J Chem. Soc.* **B** 1013 (1969); Brook, Castle, Lindray-Smith, Higgins and Morris, *J. Chem. Soc., Perkin Trans* 2,687 (1982); Lai and Prette, *Tetrahedron Lett.* (1979).

CHAPTER-V

Graft Co-polymerization of 2-Acrylamido-2-methyl-1-propanesulphonic acid (AMPS) onto Guar Gum.

1. *Structure, Chemical Composition, Properties and Uses of Guar Gum.*

2. *Graft Co-polymerization of 2-Acrylamido-2-methyl-1-propanesulphonic acid onto Guar Gum by Bromate-Mandelic acid ($BrO_3^-/C_6H_5CH(OH)COOH$) Redox Pair.*

1. STRUCTURE CHEMICAL COMPOSITION, PROPERTIES AND USES OF GUAR GUM:

Guar Gum is derived from the seed of Guar plant *cyamopsis tetragonolobus* pod bearing legune grown commercially in Pakistan, India and south western USA. During processing seed coat is removed by heating and then differential wet milling is used to separate the germ from the endosperm. The endosperm contains about 80% golactomannan and is finally ground to a fine particle size which is called Guar gum.

Structurally guar gum is D-galacto-D-mannoglycan[1]. Methylation, fragmentation and periodate oxidation show that guar gum consists of (1→4)-β-D-mannopyranosyl units with α-D-galactopyranosyl unis attached by (1→6) linkages. Enzymatic hydrolysis of guar gum gives mannobiose (4-O-β-D-mannopyranosyl-D-mannose), mannotriose and 6-O-α-D-galactopyranosyl-D-mannopyranose, showing that β-D-(1→4) linkages are present in the mannan and side chain D-galactose units are attached by α-D-(1→6) linkages. The ratio of D-galactose to D-mannose in guar gum is 1:2 with single D-galactopyranosyl uhnit side chains attached to every other D-mannopyranosyl unit[2,3] as represented in fig. 5.1. The molecular weight has been reported as 220000[4].

PROPERTIES:

1. *Viscosity:*

Guar gum forms highly viscous colloidal dispersion (solution) when hydrated in cold water, viscosities can be measured either with rotational shear type viscometer such as Brookfield synchro-Lectric or by pipette type instrument such as Ostwald viscometer. Viscosity of guar gum is dependent on time, temperature, concentration, pH, ionic strength and type of agitation. The viscosity of fully hydrated 1% guar gum solution varies almost directly with

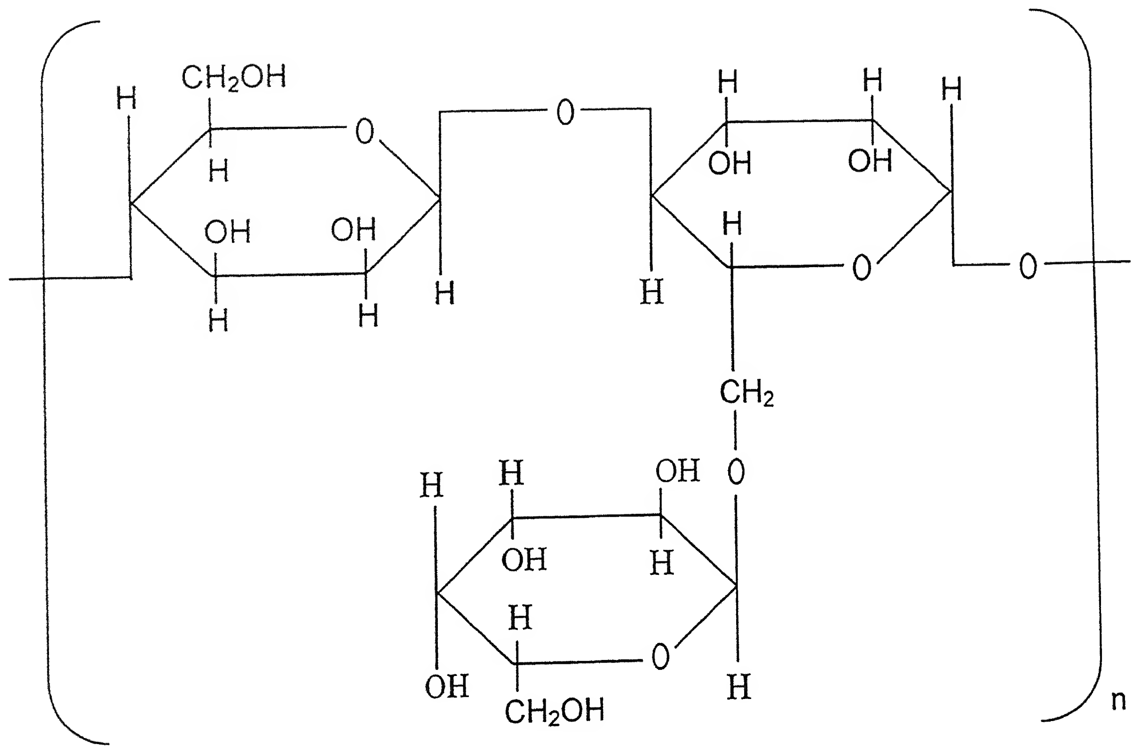
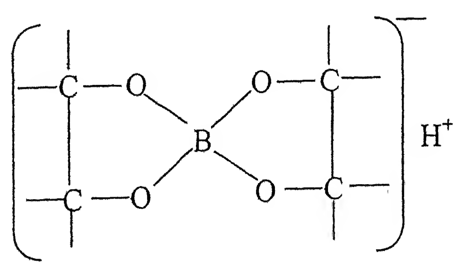


Fig. 5.1: Structure of Guar Gum

change in temperature over the range 20-80°C[5]. Guar gum solution behaves as non-Newtonian solution, mainly as a result of the complex surface attraction, at higher concentration. Guar gum is stable over a wide pH range. The non-ionic nature of the molecule is responsible for the almost constant viscosity of solution with pH's of 1-10.5. At pH's above 11, hydration is depressed and low viscosity results. Since guar gum is non-ionic, it is not susceptible to salting out, compatibility with salts is exhibited over a wide range of electrolyte concentration. For salts containing mono, di or trivalent cations stability is good and viscosity increases. Effect of particulate inclusions or fillers on rheological properties of gum guar was studied by Rayment et al.[6].

2. *Gels:*

The transformation of a colloidal solution into a coherent liquid rich system is gellation. This type of system solidifies or sets when temperature is lowered or a crosslinking agent is added. At 2-3% concentrations, it losses fluidity and becomes a gel, although it does not set into a typical structural gel, like those of gelatin or pectin until higher concentrations are reached. Small amounts of borate ion however, crosslink guar gum to form rubbery gel, which can be reversed by adjustment to an pH greater than seven, polysaccharides with numerous hydroxyl groups in cis position can form three dimensional borated gels[7]. In alkaline medium, the borate ion can react at C_2 and C_3 of the mannose units and C_3 and C_4 of the galactose side branches, which can be represented as[8]:



3. *Films:*

Guar gum forms tough, pliable films, which are sensitive to water. Palmer and Ballantyne[9] described a method for producing highly oriented films, which are elongated to 150%. The films produced from the triacetate are colourless transparent and have a tensile strength which is slightly lower than that of films of cellulose triacetate or potato amylose triacetate[10]. The films can be plasticized to make them soft and pliable.

4. *Adhesiveness:*

Guar gum solution shows very little adhesiveness in solution, which is consistent with its long straight chain singly, branched structure. This contrasts with the adhesiveness displayed by a highly branched structure, such as amylopectin. The adhesiveness of guar gum solution can be increased to some extent by conversion with acid, however, the viscosity will be reduced by this technique.

USES:

1. *Mining Industry:*

Guar gum is used in froth flotation of potash as an auxiliary reagent, depressing the gangue minerals, which might be clay, talc or shale[11,12]. Guar gum is also used as a flocculants or settling agent to concentrate ores in the mining industry By adding guar gum to the thickners, faster settling of suspended solids can be achieved. The addition of guar gum to a pulp results in the flocculation of suspended slimes or clay particles.

2. *Food:*

Guar gum is often used in foods as a thickner and a binder of free water in sauces and salad dressings. It is also used as binder of free water and as a stabilizer in ice cream[13]. Guar gum binds the free water without disturbing the

viscosity characteristics of the mix. It is also particularly suitable for use in flash pasteurization because of its rapid hydration properties[14].

3. *Cosmetics and Pharmaceuticals:*

Guar gum is used to thicken various cosmetics and pharmaceuticals[15]. It is also used as a binder and disintegrator for compressed tablets[16]. In coarse granulation guar gum is also being investigated as a bulk laxative.

4. *Paper Industry:*

The biggest industrial user of guar gum is the paper industry, it is added to the pulp, where it contributes to the hydrogen bonding between cellulose fibres[17], facilitating wet and processing and resulting in improved sheet formation and products with improved dry and wet strength.

5. *Explosives:*

In the production of a water resistant, ammonium nitrate type of explosives[18], guar gum is blended with the ingredients because of its ability to hydrate and crosslink in saturated salt solution.

6. *Petroleum Recovery:*

Guar gum is being increasingly used in various processes of petroleum such as drilling acidizing and fracturing where it serves the functions of water loss control, flocculation, suspension and turbulent friction reduction. But its use is limited because it is readily degraded by biological attack.

Modified Guar Gum and Its Uses:

Many derivatives of guar gum have been prepared and reported in the literature. These include oxidized guar gum[19], carboxymethylated guaran[20], methylated guaran[21] and many other typical carbohydrate modification.

A quite different approach to modification is grafting of synthetic polymers of different lengths and of different reactive groups to guar gum. However, the review of literature reveals that reports on modification of guar gum through grafting of vinyl monomer is scanty, Mehrotra[22] has grafted guar gum or its derivatives with acrylonitrile, acrylamide, methacrylate, methacrylamide in the presence of radical initiator compressing peroxides and polyvalent metal ions such as Ce^{+4}, Co^{+3}, Mn^{3+}, V^{5+} etc. The kinetics of grafting acrylamide on guar gum by different redox pairs was studied by Bajpai et al.[23-26]. Acrylonitrile was grafted on guar gum and average molecular weight of acrylonitrile chains grafted onto guar gum was determined at different initiator and activator concentrations[27,28]. Graft copolymerization of acrylonitrile induced by gamma ray irradiation, has been utilized to prepare superabsorbent polymers based on guar gum[29]. The effect of new eco-friendly polymeric wet end additive based on guar gum-g-polyacrylonitrile on the physical properties of paper were studied[30]. Polyacrylonitrile grafted guar-gum showed an overall improvement in all the mechanical and physical properties of the paper.

In recent years an attempt has been made successfully to graft vinyl monomers such as acrylamide, 4-vinyl pyridine, acrylic acid, methacrylamide etc. initiated by redox pairs[31-35]. The study of physical properties of guar gum-g-acrylamide reveals that it is a compromise between high drag reduction effectiveness with low shear stability of synthetic polymers and low drag reduction effectiveness with very high shear stability of polysaccharides[36,37]. Furthermore these grafted copolymers are highly resistant to biodegradation[38] and act as very efficient flocculating agent for industrial effluent containing metallic contaminants[39].

2. GRAFT COPOLYMERIZATION OF AMPS ONTO GUAR GUM BY BROMATE / MANDELIC ACID ($BrO_3^-/C_6H_5CH(OH)COOH$) REDOX PAIR:

Chemical modifications of natural macromolecules are very important to impart more desirable properties. Application of there modification reactions is a useful area in polymer chemistry. Grafting has been used as an important technique for modifying physical and chemical properties of polymers. Corn starch-g-acrylamide is useful as flocculant for treating waste water containing Hg^{++} from paper industry[40]. When acrylamide is grafted on cellulose its water retention value increases[41]. Thermal stability of starch-g-acrylamide is found to increase with acrylamide concentration[42].

The high thickening efficiency, hydrogen bonding properties, good electrolytic compatibility and low cost have resulted in guar gum being most extensively used gum in both food and industrial applications. However, it is readily degraded by biological attack, which limits its use considerably. With a view to minimize this limitation, it has been grafted with different vinyl monomers employing different initiators[43-49]. The properties and applications of grafted guar gum depend on the type of vinyl monomer grafted.

2-Acrylamido-2-methyl-1-propanesulphonic acid is characterized by its hydrophilicity and ionic character. Consequently, it has been used to prepare high swelling capacity polymer hydrogels[50] and its copolymers with some vinyl monomers such as acrylamide, methyl methacrylate and dimethylaminomethyl have been reported[51-52]. An attempt has been made to graft this monomer onto guar gum with the help of suitable redox pair. The effect of different parameters on the grafting procedure have been studied.

EXPERIMENTAL:

Materials:

2-Acrylamido-2-methyl-1-propanesulphonic acid (Sigma) was used as such. Potassium bromate (E. Merck) and Mandelic acid (E. Merck) were used as such Guar gum was received from Hindustan Gums and Chemicals Ltd., India as a gift sample. For maintaining hydrogen ion concentration sulphuric acid (E. Merck) was used. All the solutions were prepared in triple distilled water. .

Procedure for Grafting:

For each experiment guar gum solution was prepared by adding desired amount of guar gum to 50ml of triple distilled water in a reactor. The reaction was carried out under nitrogen atmosphere at constant temperature. A calculated amount of 2-Acrylamido-2-methyl-1-propanesulphonic acid, potassium bromate and, sulphuric acid solutions were added. The stream of nitrogen gas was allowed to pass through the solution in reactor and mandelic acid solution for half an hour. The reaction was initiated by the addition of mandelic acid solution. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into water methanol mixture. The precipitate was separated dried and weighed.

RESULT AND DISCUSSION:

The graft copolymer has been characterized according to Fanta's definitions as discussed earlier. The effect of H_2O_2, Fe^{2+}, H^+, 2-Acrylamido-2-methyl-1-propanesulphonic acid and guar gum concentration as well as time and temperature on grafting parameters have been studied.

Effect Of Bromate Ion Concentration:

The effect of bromate ion on grafting parameters has been studied in the

concentration range of 8.0 to 32.0×10^{-3} mol. dm^{-3} (Table-5.1). Grafting ratio, add on and conversion decrease with increase in bromate ion concentration (Figs. 5.2 & 5.3).

Effect Of Mandelic Acid Concentration:

The effect of mandelic acid on grafting reaction has been studied by varying the mandelic acid concentration from 10.0 to 30.0×10^{-3} mol dm^{-3} (Table-5.2). As the mandelic acid concentration is increased from 10.0 to 20.0×10^{-3} mol dm^{-3}, grafting ratio, add on and conversion decrease, but thereafter increase with the mandelic acid concentration (Figs. 5.4 & 5.5).

Effect Of Hydrogen Ion Concentration:

The effect of hydrogen ion on the grafting reaction has been studied by varying the H_2SO_4 concentration from 4.0 to 28.0×10^{-2} mol dm^{-3} (Table-5.3). Grafting ratio, add on and conversion decrease with increase in hydrogen ion concentration (Figs. 5.6 & 5.7). Since there is no formation of homopolymer, above observation may be explained on the basis of the fact that higher concentration of hydrogen ion reduces BrO_3^- to Br^- thereby reducing the production of primary free radicals leading to decrease in grafting parameters.

$$6H^+ + BrO_3^- + 5e \rightarrow \tfrac{1}{2} Br_2 + 3H_2O$$

$$\tfrac{1}{2}Br_2 + e \rightarrow Br^-$$

Effect Of 2-Acrylamido-2-Methyl-1-Propanesulphonic Acid:

The results of 2-Acrylamido-2-methyl-1-propanesulphonic acid variation have been summarized in Table-5.4. The data reveal that grafting ratio and add on increase on increasing the 2-Acrylamido-2-methyl-1-propanesulphonic acid concentration. Conversion however, decreases with increase in 2-Acrylamido-2-methyl-1-propanesulphonic acid concentration (Figs. 5.8 & 5.9). The increase in grafting ratio with monomer concentration may be due to the greater availability

of monomer at chain propagating site. The decrease in conversion with monomer concentration may be attributed to the increase in viscosity of the medium due to greater solubility of poly (AMPS) in water.

Effect Of Guar Gum Concentration:

The concentration of gum has been varied from 0.7 to 1.6 g dm^{-3} to study its effect on grafting and results are summarized in Table-5.5. Grafting ratio and add on decrease, while conversion increase with guar gum concentration (Figs. 5.10 & 5.11). This may be due to increase in the viscosity of the reaction medium, which hinders the movement of free radicals thereby decreasing the grafting ratio, and add on.

Effect Of Time Period:

The graft copolymerization has been studied by increasing the duration of the reaction from 60 to 150 minutes (Table-5.6). The grafting ratio, add on and conversion increase as the duration of the grafting reaction is increased (Figs. 5.12 & .13). The increase in grafting ratio may be attributed to the addition of monomer molecules to the growing grafted chains.

Effect Of Temperature:

The effect of temperature on grafting parameters has been studied at various temperatures ranging from 25 to 45°C (Table-5.7). Increase in grafting ratio, add on and conversion is observed as temperature is raised from 25 to 40°C, but decrease in these parameters is observed as the temperature is raised from 40 to 45°C (Figs. 5.14 & 5.15). The increase in grafting parameter may be attributed to the increase in the formation of active sites on account of enhanced production of primary free radicals with increase in temperature. The decrease in grafting parameters may be attributed to the premature termination of growing grafted chains by excess of free radicals at higher temperature.

EVIDENCE OF GRAFTING:

I.R. Spectra:

On comparing the IR spectra of guar gum and guar gum-g-AMPS, following additional peaks/bands in the spectra of guar gum-g-AMPS has been observed.

Abroad band in the region 1675-1625 cm^{-1} is obtained due to overlapping of N-H bending vibrations band and C=O stretching vibrations band. A weak band at 1409.1cm^{-1} appeared due to C-N stretching vibrations. These bands/peaks confirm the grafting of AMPS onto guar gum backbone.

Thermal Degradation Behaviour of Guar Gum:

The degradation of guar gum started at about 230°C, it is a single step degradation reaction. The rate of weight loss increases on increasing the temperature upto 310°C, but decreases thereafter. About 68% weight loss occured between 200 to 400°C. At 800°C only 5% char yield is obtained. Nearly 75% of guar gum degraded at 400°C (Table 5.9). Therefore final decomposition temperature (FDT) is very low, i.e. 320°C. Polymer decomposition temperature (PDT), T_{max} and integral procedural temperature (IPDT) of guar gum is 280, 310 and 318.8°C respectively (Tale 5.8). The linear relationship between Δlog dw/dt vs. Δlog W, where dw/dt is rate of weight loss and W is residual weight can not be obtained. This is because, degradation of guar gum is quite complex and starts with depolymeriztion through random chain scession associated with degradation followed by molecular rearangements (Fig. 5.16).

Thermal Degradation Behaviour of Guar gum-g-AMPS:

Guar gum-g-AMPS graft copolymer has been obtained by grafting AMPS onto guar gum using BrO_3^-/mandelic acid redox pair.

The graft copolymer began to degrade at about 157.0°C. The rate of weight loss increases rapidly with temperture upto 200°C, but beyond 200°C, the rate of weight loss is not so pronounced. Therefore the temperature at which maximum weight loss occured is rather low i.e. 182°C. The degradation appears to be two-stage process i.e. from 182°C to 340.2°C and from 340.2 to 512.2°C. About 45% weight loss was observed in the temperature range 100-500°C (Table 5.10) and a char yield of 35% was obtained at 840°C. The polymer decomposition temperature (PDT), final decomposition temperature (FDT) and integral procedural temperature (IPDT) were found to be 157, 340.2 and 220.3°C respectively (Table 5.8 & Fig. 5.17).

MECHANISM:

$OH^{\bullet}$, $C_6H_5-\underset{OH}{\overset{\bullet}{C}}-COOH$ and $Br^{\bullet}$ radicals are generated by the interaction of $C_6H_5CH(OH)COOH$ and BrO_3^-. These radicals represented by $R^{\bullet}$, abstract hydrogen from guar gum molecule producing guar gum radical ($GO^{\bullet}$). The monomer molecules, which are in close vicinity of the reaction sites, become acceptor of guar gum radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules. These grafted chains terminate by coupling to give graft copolymer.

The reaction mechanism can be represented by the following steps:

$$C_6H_5\,CH(OH)COOH + BrO_3^- \rightarrow C_6H_5-\underset{OH}{\overset{\bullet}{C}}-COOH + BrO_2^- + OH^{\bullet}$$

$$C_6H_5\,CH(OH)COOH + BrO_2^- \rightarrow C_6H_5-\underset{OH}{\overset{\bullet}{C}}-COOH + BrO^- + OH^{\bullet}$$

$$C_6H_5\,CH(OH)COOH + BrO^- \rightarrow C_6H_5-\underset{OH}{\overset{\bullet}{C}}-COOH + Br^{\bullet} + OH^-$$

$$C_6H_5\,CH(OH)COOH + BrO^{-} \rightarrow C_6H_5-\underset{\displaystyle OH}{\overset{\bullet}{C}}-COOH + Br^{-} + OH^{\bullet}$$

$$M + R^{\bullet} \rightarrow RM^{\bullet}$$

$$GOH + RM^{\bullet} \rightarrow GO^{\bullet} + RMH$$

$$(\text{Where } R^{\circ} = OH^{\bullet},\ C_6H_5-\underset{\displaystyle OH}{\overset{\circ}{C}}-COOH,\ Br^{\bullet})$$

Initiation:

$$GO^{\bullet} + M \rightarrow GOM_1^{\bullet}$$

Propagation:

$$GOM_1^{\bullet} + M \rightarrow GOM_2^{\bullet}$$

$$GOM_2^{\bullet} + M \rightarrow GOM_3^{\bullet}$$

....

....

....

$$GOM_{n-1}^{\bullet} + M \rightarrow GOM_n^{\bullet}$$

Termination:

$$GOM_n^{\bullet} + GOM_m^{\bullet} \rightarrow \text{graft copolymer}$$

Table 5.1

Effect of Bromate Ion

[Mandelic acid] = 20.0 x 10^{-3} mol dm^{-3}; [AMPS] = 4.0 x 10^{-2} mol dm^{-3}; [H^+] = 16.0x10^{-2} mol dm^{-3}; [Guar Gum] = 1.0 g dm^{-3}; Time = 120 min; Temp = 35°C.

S.N.	[BrO_3^-]x10^3 mol dm^{-3}	% G	% A	% C
1.	8.0	154.7	60.7	18.7
2.	14.0	135.4	57.5	16.3
3.	20.00	101.2	50.3	12.2
4.	26.0	90.3	47.5	10.9
5.	32.0	78.6	44.0	9.5

Table 5.2

Effect of Mandelic Acid

.[H^+] = 16.0 x 10^{-2} mol dm^{-3}; [AMPS] = 4.0 x 10^{-2} mol dm^{-3}; [BrO_3^-] = 20x10^{-3} mol dm^{-3}; [Guar Gum] = 1.0 g dm^{-3}; Time = 120 min; Temp = 35°C.

S.N.	[MA] x10^3 mol dm^{-3}	% G	% A	% C
1.	10.0	134.0	57.3	16.7
2.	15.0	120.6	54.7	14.6
3.	20.0	101.2	50.3	12.2
4.	25.0	120.3	54.6	14.5
5.	30.0	135.8	57.6	16.4

Table 5.3

Effect of Hydrogen Ion

[Mandelic acid] = 20.0 x 10^{-3} mol dm^{-3}; [AMPS] = 4.0 x 10^{-2} mol dm^{-3}; [BrO_3^-] = 20x10^{-3} mol dm^{-3}; [Guar Gum] = 1.0 g dm^{-3}; Time = 120 min; Temp = 35°C.

S.N.	[H^+]x10^2 mol dm^{-3}	% G	% A	% C
1.	4.0	125.3	55.6	15.1
2.	10.0	110.2	52.4	13.2
3.	16.0	101.2	50.3	12.2
4.	22.0	85.6	46.1	10.3
5.	28.0	70.8	41.5	8.5

Table 5.4

Effect of AMPS

[Mandelic acid] = 20.0 x 10^{-3} mol dm^{-3}; [BrO_3^-] = 20.0 x 10^{-3} mol dm^{-3}; [H^+] = 16.0x10^{-2} mol dm^{-3}; [Guar Gum] = 1.0 g dm^{-3}; Time = 120 min; Temp = 35°C.

S.N.	[AMPS]x10^2 mol dm^{-3}	% G	% A	% C
1.	2.0	74.0	42.5	17.8
2.	4.0	101.2	50.3	12.2
3.	6.0	125.6	55.6	10.1
4.	8.0	135.7	57.6	8.2

See References On Page No. 127-129

Table 5.5

Effect of Guar Gum

[Mandelic acid] = 20.0 x 10^{-3} mol dm^{-3}; [AMPS] = 4.0 x 10^{-2} mol dm^{-3}; [H^+] = 16.0x10^{-2} mol dm^{-3}; [BrO_3^-] = 20.0x10^{-3} mol dm^{-3}; Time = 120 min; Temp = 35°C.

S.N.	[Guar Gum] g dm^{-3}	% G	% A	% C
1	0.7	128.6	56.3	10.8
2.	1.0	101.2	50.3	12.2
3.	1.3	86.5	46.3	29.3
4.	1.6	64.2	39.1	31.7

Table 5.6

Effect of Time Period

[Mandelic acid] = 20.0 x 10^{-3} mol dm^{-3}; [AMPS] = 4.0 x 10^{-2} mol dm^{-3}; [H^+] = 16.0x10^{-2} mol dm^{-3}; [Guar Gum] = 1.0 g dm^{-3}; [BrO_3^-] = 20.0x10^{-3} mol dm^{-3}; Temp = 35°C.

S.N.	Time (Min)	% G	% A	% C
1.	60	70.8	41.5	8.5
2.	90	85.6	46.1	10.3
3.	120	101.2	50.3	12.2
4.	150	114.6	53.4	13.8

See References On Page No. 127-129

Table 5.7

Effect of Temperature

[Mandelic acid] = 20.0 x 10^{-3} mol dm^{-3}; [AMPS] = 4.0 x 10^{-2} mol dm^{-3}; [H^+] = 16.0x10^{-2} mol dm^{-3}; [BrO_3^-] = 20.0x10^{-3} mol dm^{-3}; [Guar Gum] = 1.0 g dm^{-3}; Time = 120 min;

S.N.	Temp °C	% G	% A	%C
1.	25	70.4	41.3	8.4
2	30	89.3	46.8	10.7
3.	35	101.2	50.3	12.2
4.	40	132.6	57.0	15.9
5.	45	115.7	53.7	13.9

Table 5.8

THERMOGRAVIMETRIC ANALYSIS OF GRAFT COPOLYMER

Sample Code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
G_1	280.0	320.0	310.0	318.8
G_2	157.0	340.2	182.0	220.3

Table 5.9

DECOMPOSITION TEMPERATURE (T°D)

Sample	T°D (°C) at following weight loss						
	10%	20%	30%	40%	50%	60%	70%
G_1	262.0	286.0	296.0	300.0	306.0	314.0	348.0
G_2	168.0	184.0	216.0	320.0	448.2	650.0	--

See References On Page No. 127-129

Table 5.10

DECOMPOSITION TEMPERATURE (T°D)

Temp (°C)	Weight loss (%)	
	G_1	G_2
100	3.0	0.6
200	7.0	24.0
300	35.0	33.5
400	75.0	42.4
500	81.0	47.1
600	88.0	50.6
700	92.0	54.1
800	95.0	55.6

G_1 = Guar Gum

G_2 = Guar gum-g-AMPS(BrO_3^-/Mandelic Acid)

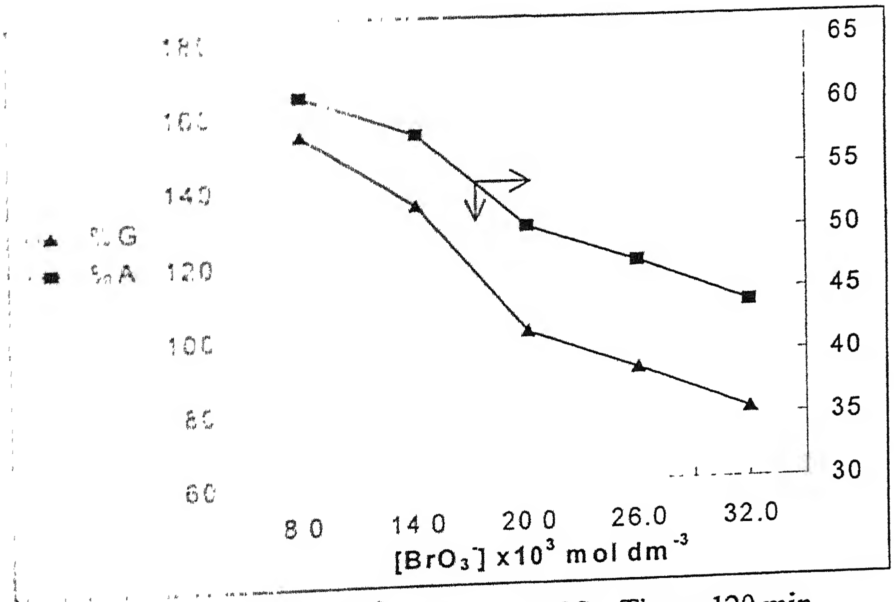


Figure 5.2 [MA] 20.0 ×10^{-3} mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] 4.0 ×10^{-2} mol dm^{-3} ; [H^+] = 16.0×10^{-2} mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

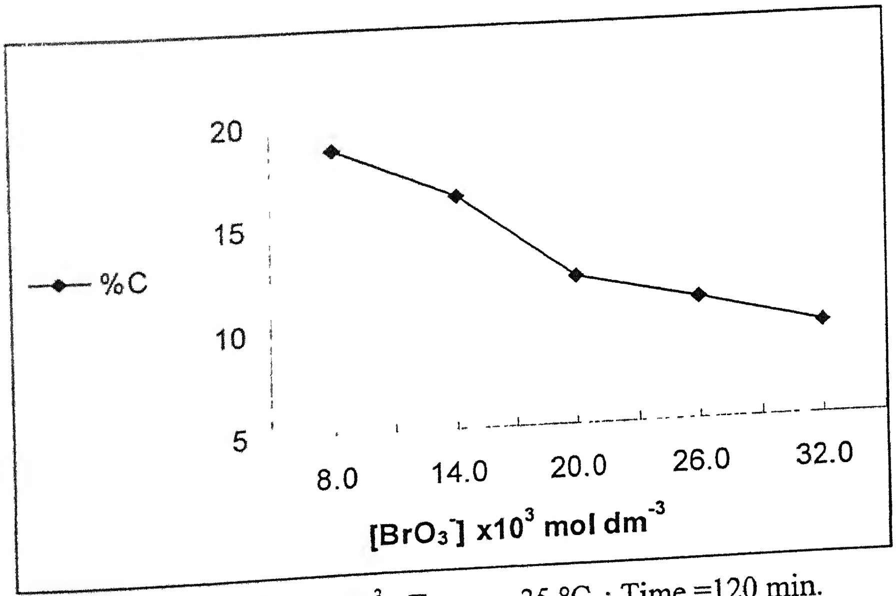


Figure 5.3 [MA] = 20.0 ×10^{-3} mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0 ×10^{-2} mol dm^{-3} ; [H^+] = 16.0×10^{-2} mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

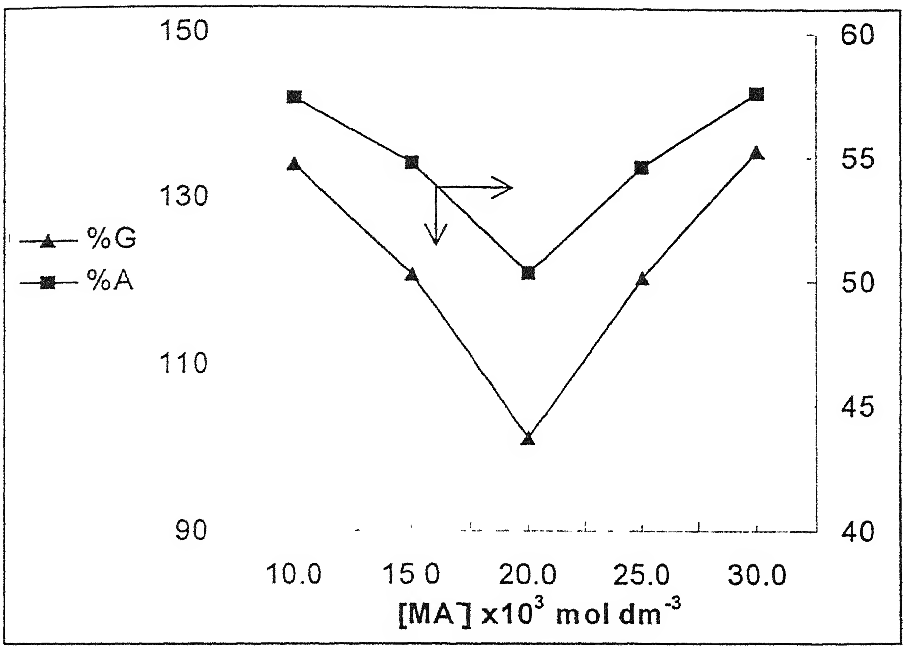


Figure 5.4 $[BrO_3^-]$ = 20.0 $\times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0 $\times 10^{-2}$ mol dm^{-3} ; $[H^+]$ = 16.0$\times 10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 dm^{-3} .

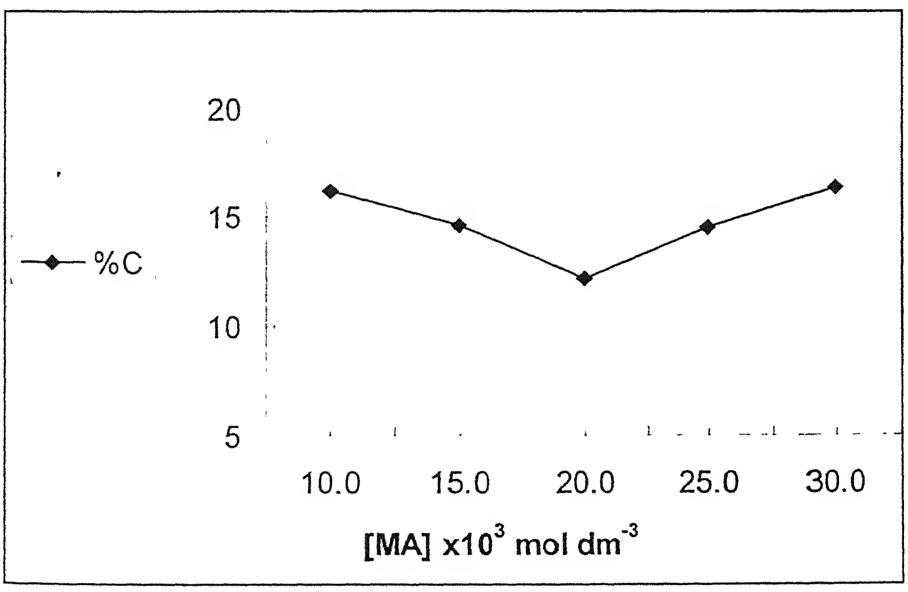


Figure 5.5 $[BrO_3^-]$ = 20.0 $\times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0 $\times 10^{-2}$ mol dm^{-3} ; $[H^+]$ = 16.0$\times 10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 dm^{-3} .

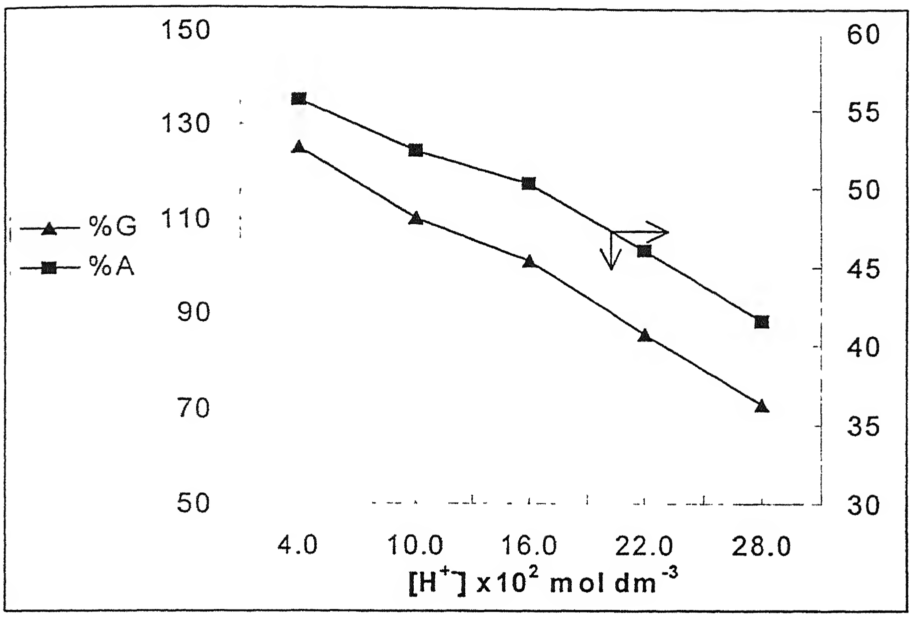


Figure 5.6 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0×10^{-2} mol dm^{-3} ; [MA] = 20.0×10^{-3} mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

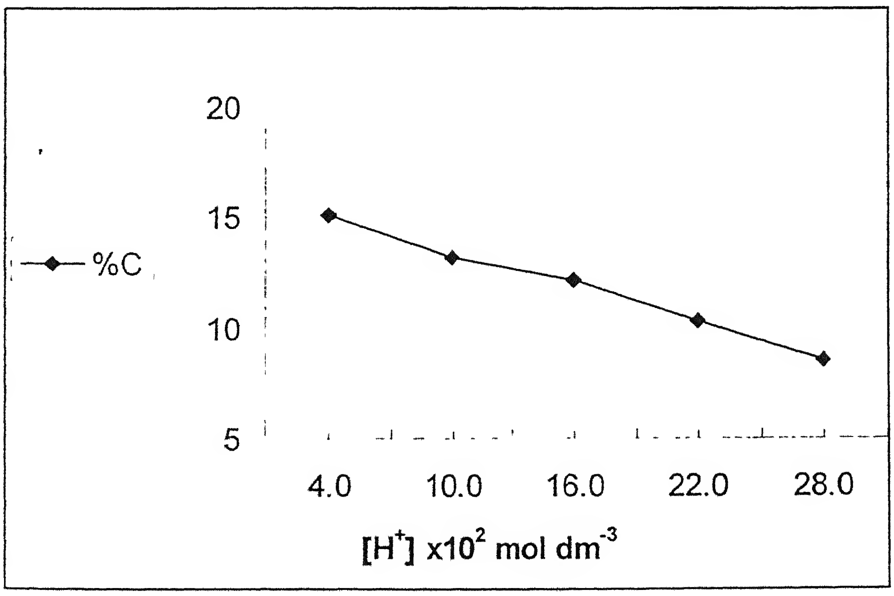


Figure 5.7 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0×10^{-2} mol dm^{-3} ; [MA] = 20.0×10^{-3} mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

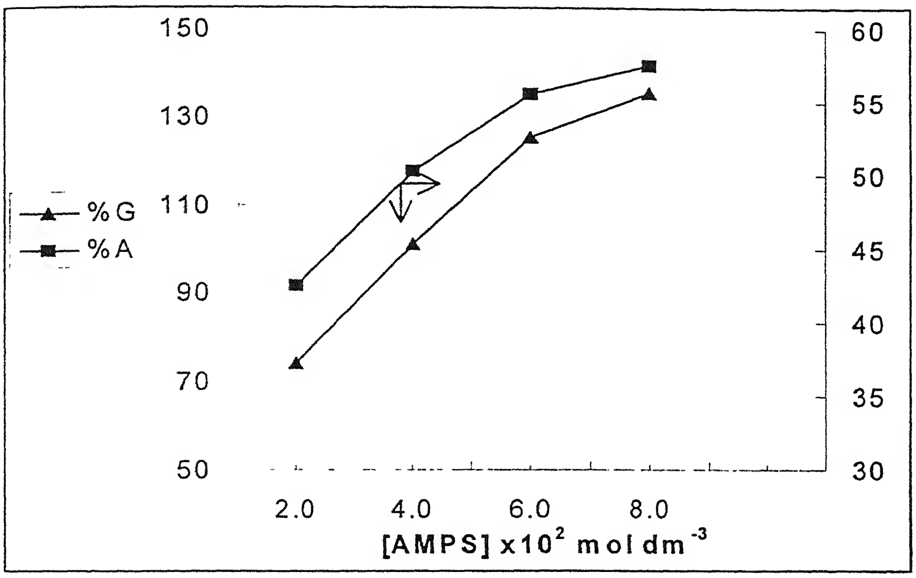


Figure 5.8 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min.
$[H^+] = 16.0 \times 10^{-2}$ mol dm^{-3} ; $[MA] = 20.0 \times 10^{-3}$ mol dm^{-3} ; [GOH] = 1.0 g dm^{-3}

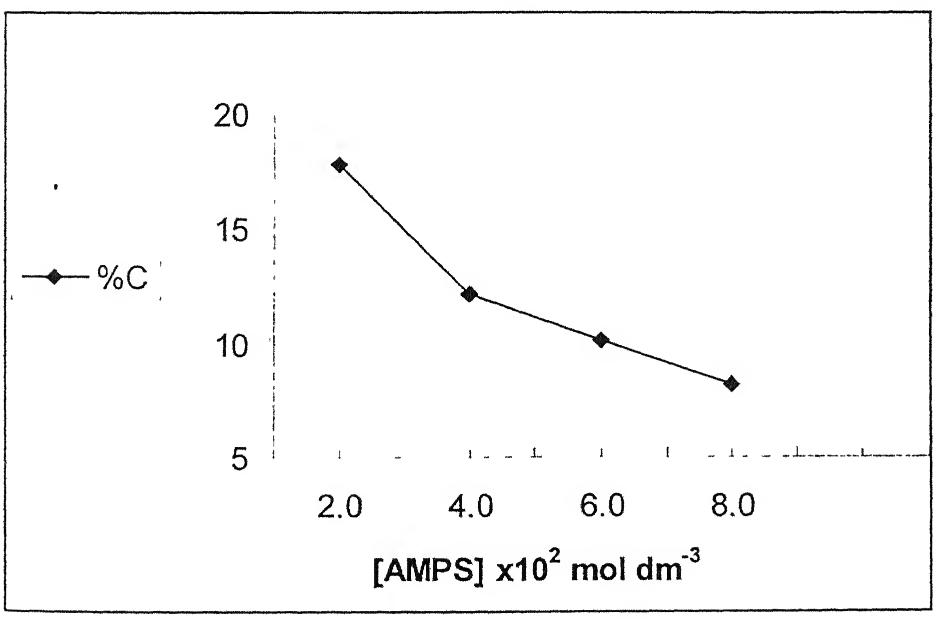


Figure 5.9 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min.
$[MA] = 20.0 \times 10^{-3}$ mol dm^{-3} ; $[H^+] = 16.0 \times 10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 g dm^{-3}

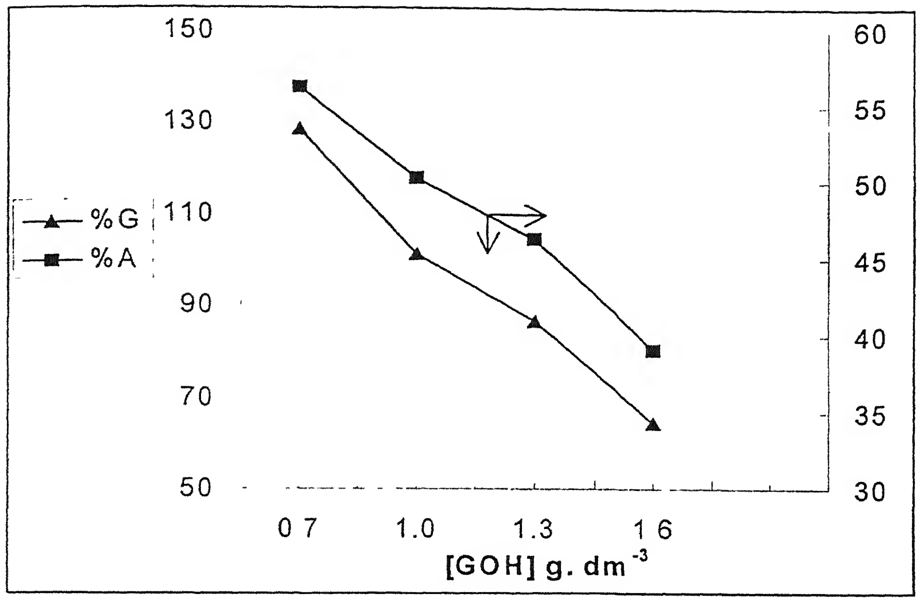


Figure 5.10 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0×10^{-2} mol dm^{-3} ; $[H^+] = 16.0 \times 10^{-2}$ mol dm^{-3} ; [MA] = 20.0×10^{-3} mol dm^{-3} .

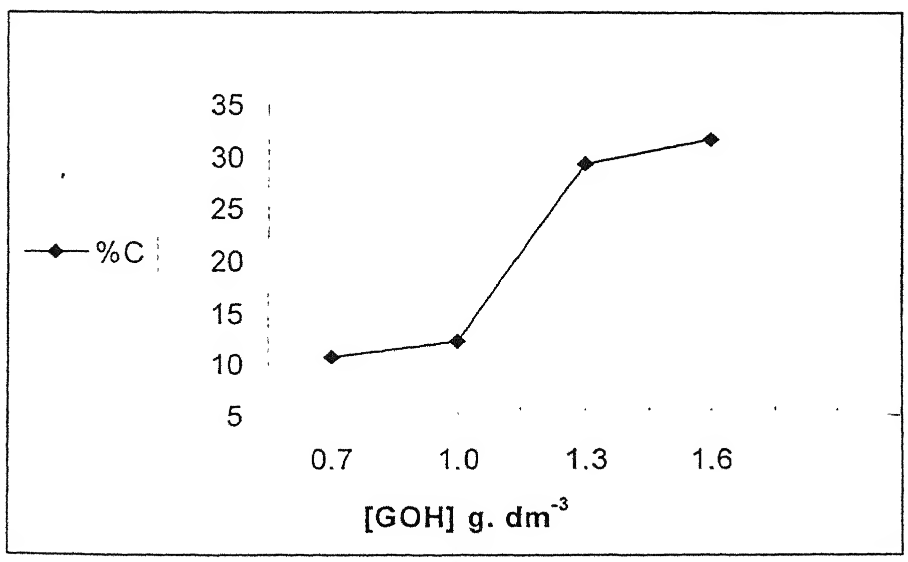


Figure 5.11 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; Time =120 min. [AMPS] = 4.0×10^{-2} mol dm^{-3} ; $[H^+] = 16.0 \times 10^{-2}$ mol dm^{-3} ; [MA] = 20.0×10^{-3} mol dm^{-3} .

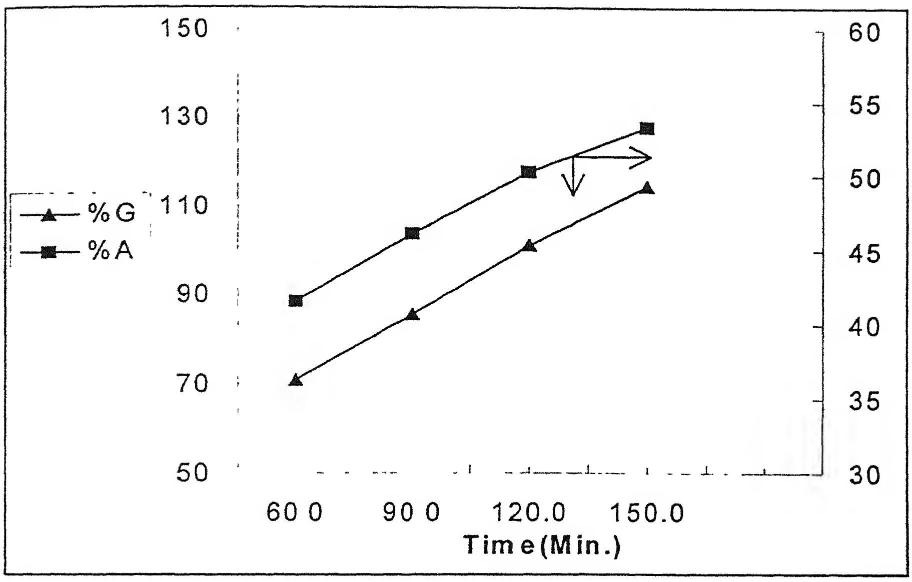


Figure 5.12 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; [MA]=20.0×10^{-3} mol dm^{-3} [AMPS] = 4.0×10^{-2} mol dm^{-3} ; $[H^+] = 16.0 \times 10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

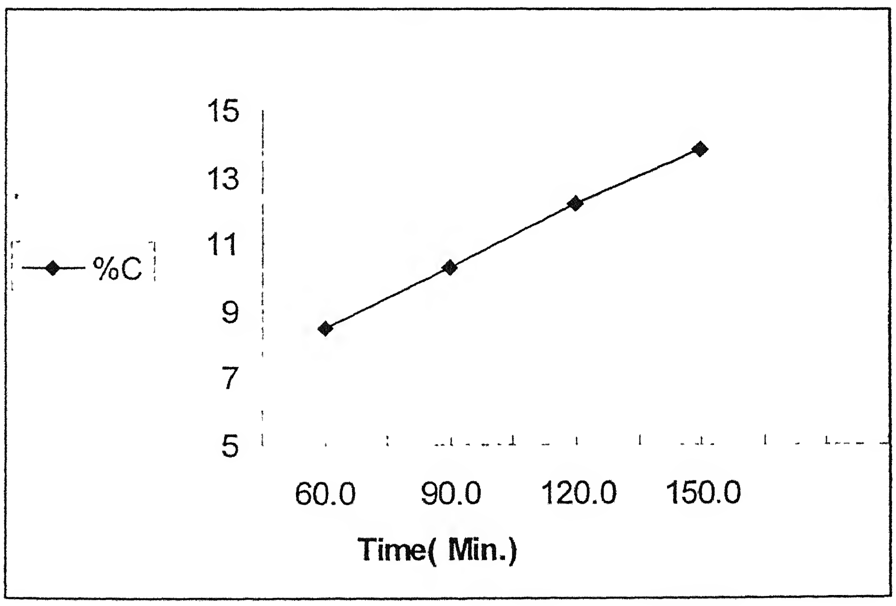


Figure 5.13 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; Temp. = 35 °C ; [MA]=20.0×10^{-3} mol dm^{-3} [AMPS] = 4.0×10^{-2} mol dm^{-3} ; $[H^+] = 16.0 \times 10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

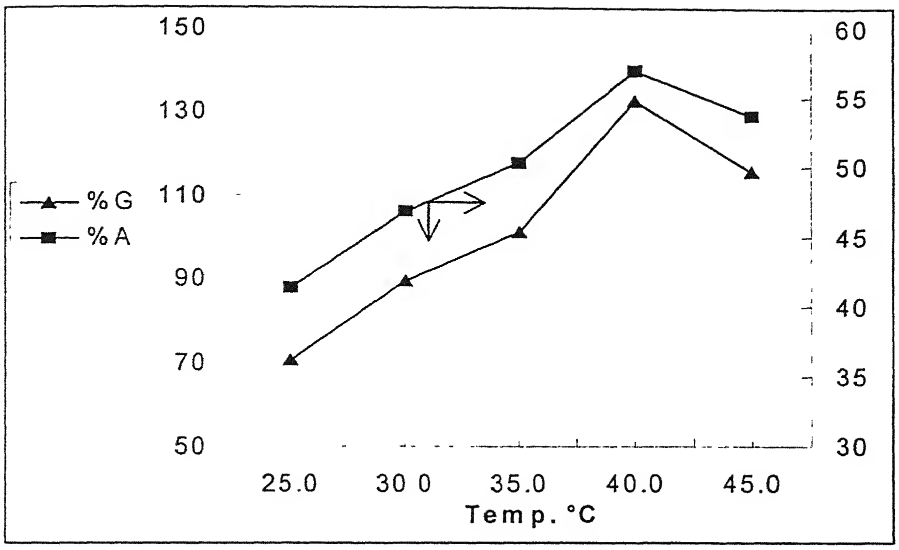


Figure 5.14 $[BrO_3^-] = 20.0 \times 10^{-3}$ mol dm^{-3} ; ; $[MA]=20.0\times10^{-3}$ mol dm^{-3} ; Time =120 min. $[AMPS] = 4.0 \times10^{-2}$ mol dm^{-3} ; $[H^+] = 16.0\times10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

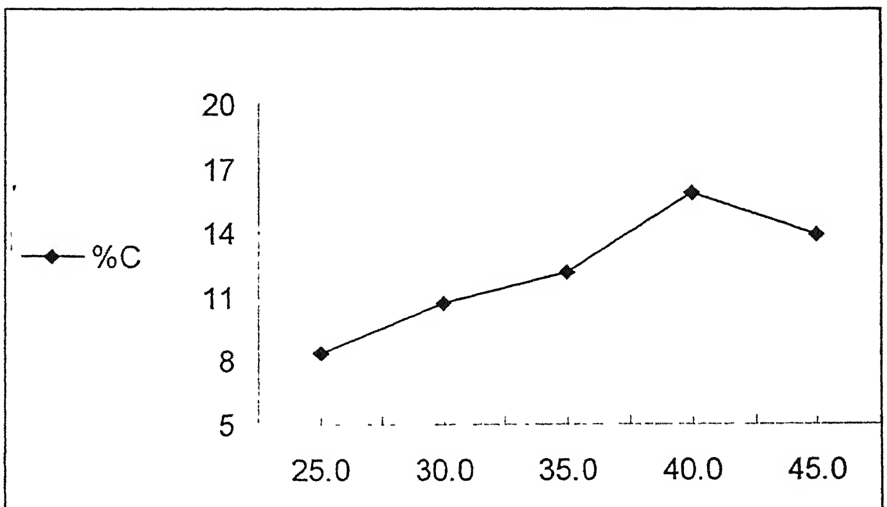


Figure 5.15 $[BrO_3^-] = 20.0 \times10^{-3}$ mol dm^{-3} ; $[MA]=20.0\times10^{-3}$ mol dm^{-3}; Time =120 min. $[AMPS] = 4.0 \times10^{-2}$ mol dm^{-3} ; $[H^+] = 16.0\times10^{-2}$ mol dm^{-3} ; [GOH] = 1.0 g dm^{-3} .

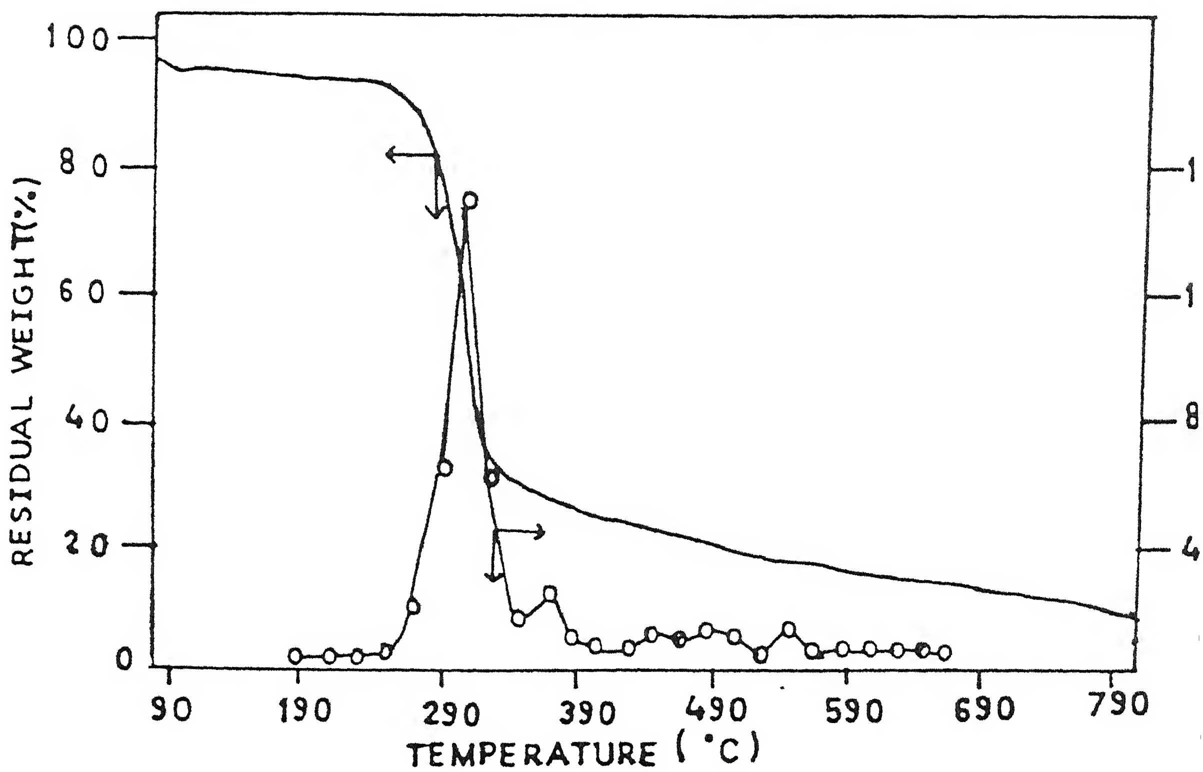


Fig. 5.16 : Thermogravimetric Trace of Guar Gum

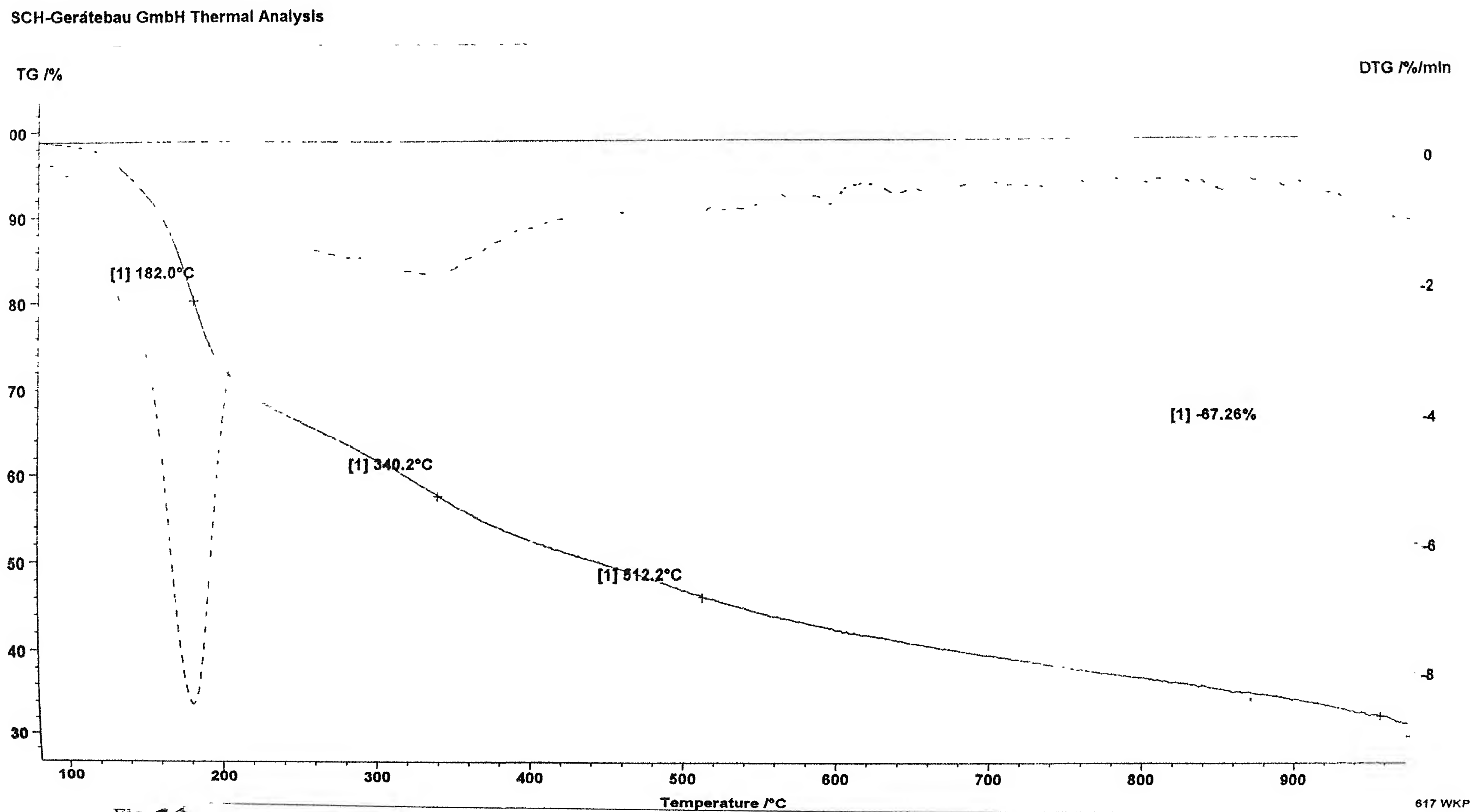


Fig 5.17 : Thermogravimetric Trace of Guar Gum-g-AMPS

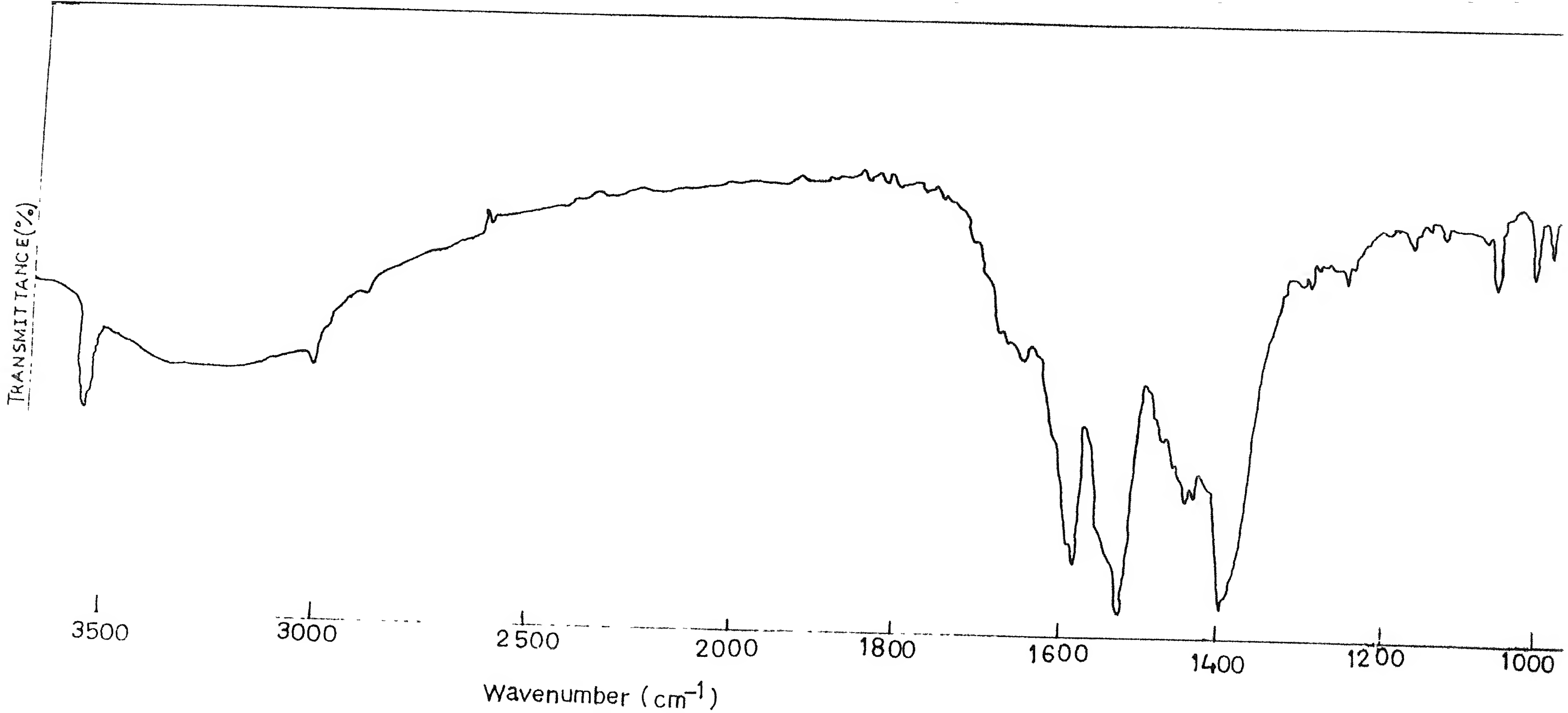
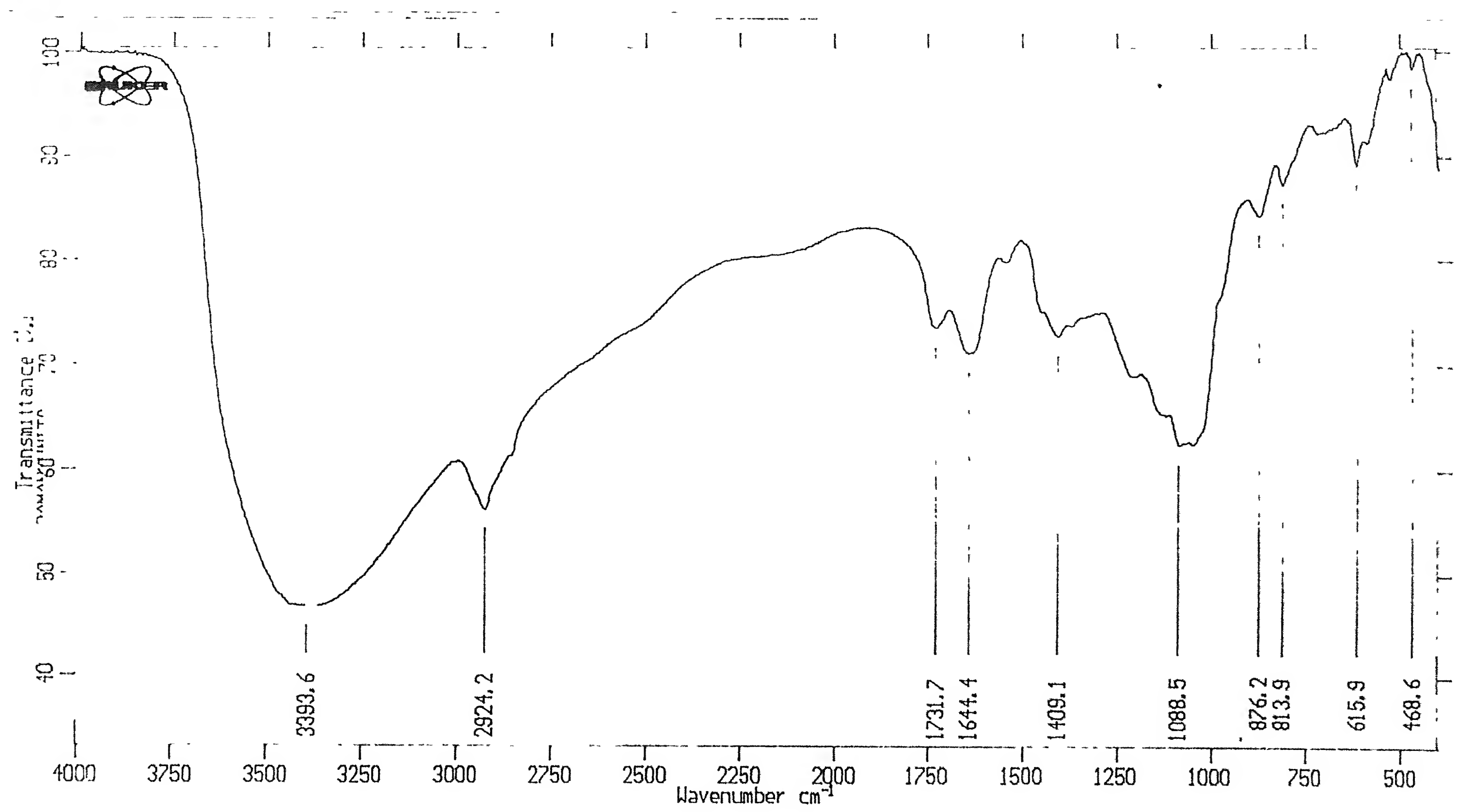


Fig 4 I R Spectra of Guar gum



SPECTRUM : WORK.4
DATE : 28/ 2/2001
TIME : 14:44:37
RESOLUTION : 4.0 cm-1

Guar gum -g- AMPS.

SAMPLE : 466-S
TECHNIQUE : KBr PELLET
USER : T.LALITHA
INSTRUMENT : IFS66V

REFERENCES

1. Seaman, J.K.; *'Handbook of water soluble gums and resins'* McGraw Hill, New York **(1980)**, 96-1.
2. Whistler, R.L. and Smart, C.L.; *'Polysaccharide Chemistry', Academic Press* Inc., New York, 5296 **(1953)**.
3. Boggs, A.D.; *Masters Thesis, Pudue University, Lafayette, Indiana* **1949.**
4. Ahmad, Z.F. and Whistler, R.L.; *J. Am. Chem. Soc.* **72,** 2524 **(1950).**
5. Devel, H.; Neukom, H. and Weber, F.; *Nature* **161,** 96 (1948).
6. Rayment, P.; Ross Murphy; Simon, B.; Ellis, P.R.; *Carbohydr. Polym.* **28(2)**, 121 (1995).
7. Isbell, H.S.; Brewster, J.F.; Holt, N.B.; Frush, H.L.; *J. Res. Natl. Bur standards* **40**, 129 (1948).
8. Diel, H.; *Chem Revs.* **21**, 39 (1937).
9. Palmer, K.J. and Ballantyne, M.; *J. Am. Soc.* **72,** 736 (1950).
10. Smart, C.L.; Whistler, R.L.; *J. Polym. Sci.* **4,** 87 (1949).
11. Atwood, G.E.; Bourne, D.J.; *Eng. Mining* **5,** 1099 (1953).
12. Atwood, G.E.; Bourne, D.J.; *U.S. Patent* 2,696,912 **(1954).**
13. Werben, S. J.; *U.S. Patent* 2,502,397 **(1950).**
14. McKierman, R.J.; Paper Presented at the *Michigan Dairy Manufacturers Annual Conference, East Lansing, Mich,* **Nov. 7, 1957.**
15. Hutchins, H.H.; Singiser, R.E.; *J. Am. Pharm Assoc. Pract. Pharm. Ed.* **16,** 226 (1955).
16. Eartherton, L.E.; Platz, P.F.; Crosgrove, F.P.; *Drug Standards,* 2342 (1955).

17. Swanson, J.W.; *Tappi*, **39**, 257 (1956).

18. Taylor, W.J.; *U.S. Patent* 2, 654, 666 **(1953)**.

19. Swanson, J.W.; *U.S. Patent* 2, 44, 412 **(1948)**.

20. Moc. A.O. *U.S. Pantent* 2, 477, 544 **(1949)**.

21. Ahmad, Z.F.; Whister, R.L.; *J Am. Chem. Soc.* **72,** 2524 (1954).

22. Mehrotra, R.; *Indian IN.* 155,091 *(Cl/08F25/00)* **(1984).**

23. Bajpai, U.D.N.; Rai, S.; *J. Appl. Polym. Sci.* **35(5),** 1169 (1988).

24. Bajpai, U.D.N.; Jain, A.; Bajpai, A.K.; *Acta Polym.* **41 (11)**, 577 (1990).

25. Bajpai, U.D.N.; Jain, A.; Rai, S.; *J. Appl. Polym. Sci.* **39 (11-12)**, 2187 (1990).

26. Bajpai, U.D.N.; Jain, A.; *Polym. Int.* **31(1)**, 1 (1993).

27. Ravel, D.K.; Patel, R.G.; Patel, V.S.; *Starch/Starke* **40 (2)**, 66 (1988).

28. Naidoo, S.; Joff, R.N.; Eberhand, W.; *Angew. Makromol. Chem.* **156,** 59 (1980).

29. Lokhande, H.T.; Varadrajan, P.V.; Iyer, V.; *J. Appl. Polym. Sci.* **45 (11)**, 2031 (1992).

30. Varadrajan, P.V.; Shaikh, A.J.; Lokhande, H.T.; *Trends Carbohydr. Chem. Carbohydr. Conf. 9th Jan. 1993 (Pub. 1995)*, 147 Ed. Soni, Purshottam L.; Surya International Publications.

31. Kunj Behari, Kavita Taunk, Mala Tripathi; *Polymer Preprint (ACS)* **37 (2)**, 268 (1996).

32. Kunj Behari, Kavita Taunk; *Ind. J. Chem. Tech.* **4(3)**, 141 (1997).

33. Kunj Behari, Kavita Taunk, Rima Das; *Polym. Int.* **46(2)**, 126 (1998).

34. Kunj Behari, Kavita Taunk, Mala Tripathi; J. Appl. Polym. Sci. **71**, 739 (1999).

35. Kunj Behari, Kavita Taunk, Mala Tripathi; *Polym. Int.* **49**, 153 (2000).

36. Singh, R.P.; Deshmukh, S.R. and Majumdar, S.K. in *Proceedings of X Congress on Rheology, Sydney* **(1988)**.

37. Deshmukh, S.R.; Singh, R.P.; Chaturvedi, P.N.; *J. Appl. Polym. Sci.* **30**, 4013 (1985).

38. Deshmukh, S.R., Singh, R.P.; *J. Appl. Polym. Sci.* **33**, 1963 (1987).

39. Singh, R.P.; Jain, S.K.; Lal, N.; *Polymer Science Contemporary Themes* **Vol. II**, 716 (1991).

40. Wu, G.S.; Yanxia, LO.; Zhaing, G.; *Chin Julin Dexue Ziren Kexue Xueba* **3**, 123 (1988).

41. Ranby, B. and Zuchowska, D.; *Polym. J.* **19(5)**, 623 (1987).

42. Singh, O.P.; Sandle, N.K. and Varma, I.K.; *Die Angewandte Makro molekulare Chemie;* **121**, 187 (1984).

43. Mehrotra, R.; *Indian I.N.* 155091 **(1984)**.

44. Lokhande, H.T.; Varadragan, P.V.; Iyer, V.; *J. Appl. Polym. Sci.* **45** (11), 2031 (1992).

45. Naidoo, S.; Joffe, R. Neuse, E.W.; *Angew. Makromol. Chem.* **156**, 59 (1988).

46. Ravel, D.K.; Patel, R.G.; Vithal, S.; *J. Appl. Polym. Sci.* 35 (8), 2201 (1988).

47. Ravel, D.K. Patel, R.G.; Patel, V.S.; *Starch/Starke,* **40(2)**, 66 (1988).

48. Bajpai, U.D.N.; Jain, A.; Rai, S.; *J. Appl. Polym. Sci.* 39 (11-12), 2189 (1990)

49. Bajpai, U.D.N.; Jain, A.; *Polym. Int.* 31(1), 1(1993).

50 Kulicke, W.M.; Nottlemann, H.; Aggour, Y.A. and Elsabee, M.Z.; *Polym. Mat. Sci. Eng.* **61**,393 (1989).

51. Aggour, Y.A.; *Polym. Deg. Stab.* **44**, 71 (1994).

52 Aggour, Y.A.; *Polym. Deg. Stab.* **45**, 273 (1994).

PUBLICATION

- Graft copolymerization of acrylamide onto xanthan gum using Fe^{2+}/BrO_3^- redox pair.

  Kunj Behari, Peeyoosh Kant Pandey, Rajesh Kumar, Kavita Taunk; Carbohydrate Polymers, ***46(2)****, 185-189 (July 2001).*

- Studies of graft copolymerization of methacrylamide onto guar gum using Cr^{6+}/ Malonic Acid redox pair.

  Kunj Behari, Peeyoosh Kant Pandey, Rajesh Kumar, Mala Tripathi; J. Macromolecular Chemistry & Physics, ***202****, 2001 (In press).*

- Studies of graft copolymrization of acrylic acid onto guar gum using V^{+5}/ mercaptosuccnic acid redox pair.

  Kunj Behari, Peeyoosh Kant Pandey, Mala Tripathi, Kavita Taunk; Ind. J. Chem. Technology (in press)

- Graft copolymerization of acrylic acid onto xanthan gum using PMS/Fe^{2+} redox pair.

  Kunj Behari, Peeyoosh Kant Pandey; J. Appl. Polym. Sci. (Communicated).